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EFFECT OF DIAGENESIS UPON CLAY MINERAL CONTENT OF INTERLAMINATED DESMOINESIAN SANDSTONES AND SHALES IN OKLAHOMA

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DAVID P. BUCKE, JR.

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EFFECT OF DIAGENESIS UPON CLAY MINERAL CONTENT OF INTERLAMINATED DESMOINESIAN SANDSTONES AND SHALES IN OKLAHOMA

APPROVED BY

Stanley J. Mankin

David B. Kitts

Harvey P. Klott

Arthur J. Myers

Stanley C. Black

DISSERTATION COMMITTEE

ABSTRACT

EFFECT OF DIAGENESIS UPON CLAY MINERAL CONTENT OF INTERLAMINATED DESMOINESIAN SANDSTONES AND SHALES IN OKLAHOMA

Closely interlaminated sandstones and shales from Desmoinesian deltaic strata have been investigated to determine the relative importance of diagenetic and detrital origin of constituent clay minerals. Close association of the two lithologic types eliminates many parameters which could otherwise have varying effects upon mineral content. Subsurface samples were studied using various x-ray diffraction and x-ray fluorescence techniques in addition to thin-section observation.

Authigenic mineral formation is quantitatively unimportant. Bulk chemical analyses show little variance between sands and shales other than those associated with expected detrital differences. Permeability is the basic factor controlling the amount of diagenesis that occurs.

Consistent differences in relative amounts of chlorite, illite, and kaolinite are present between sands and shales. Illite and chlorite are of detrital origin whereas a significant portion of the kaolinite has been formed diagenetically. Illite is the dominant clay mineral in all shales and most sands investigated, but is relatively more abundant in shales and in finer size fractions of both sands and shales. Chlorite distribution is variable, not being directly related to grain size, because this mineral is present both as clay and in metamorphic rock fragments. Kaolinite is a much more important constituent in sands, a difference attributed to authigenic formation of this mineral in the more permeable sands.

Authigenic kaolinite formation was possible because four coexisting factors were present: organic material to help maintain a low pH through bacterial activity, potassium feldspars as a source of aluminum and silicon, partly degraded illite as an efficient "sink" for potassium released during feldspar decomposition, and water-filled pore space allowing aqueous solution chemistry to proceed and to provide growth space for the kaolinite. The formation of authigenic kaolinite did not require long-distance transport of necessary ions, all ingredients being present in situ.

Additional minerals were formed during diagenesis, especially in the sands. The sequence of formation of these authigenic components being: quartz overgrowths, kaolinite, calcite, dolomite, and finally pyrite-siderite. An additional initial authigenic mineral, "hydrotroilite," is proposed.

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CONTENTS

Page

ILLUSTRATIONS

EFFECT OF DIAGENESIS UPON CLAY MINERAL CONTENT OF INTERLAMINATED DESMOINESIAN SANDSTONES AND SHALES IN OKLAHOMA

INTRODUCTION

Literature dealing with the clay-mineral content of sediments and rocks is abundant. An unsolved problem frequently discussed is the origin of the clay-mineral suites present in the various lithologies. Most investigators have agreed that both detrital and diagenetic processes are operative, but the problem of which is more effective within a given environment is met with little accord.

Support for Detrital Origin

One of the leading proponents for a dominant detrital or allogenic origin of clay minerals is C. E. Weaver who concludes (1958a, p. 254) ". . . that the great majority of clay minerals in sedimentary rocks are detrital in origin, strongly reflect the character of their source material, and are only slightly modified in their depositional environments." The same writer (Weaver, 1959) gives an excellent review of clay petrology in both modern and ancient sediments, again emphasizing detrital control of the clay minerals. The European literature has been surveyed by Riviere (1953, in Weaver, 1959) with the same conclusions being reached. Some Russian investigators have also supported the detrital origin of clays. An example is the conclusion reached by

Yurevich (1961, p. 821) from his studies of the Akchagylian deposits of the Pribalkhan region; "The clear connection that exists between the granulometry of the sediment and the composition of the clay minerals and the tectonic situation . . . enables us to assume that . . . the clay minerals did not undergo any significant changes during the stages of sedimentogenesis and diagenesis."

After study of cores taken from the North Pacific, Griffin and Goldberg (1963, p. 739) conclude ". . . the homogeneous distribution of clay minerals with depth in any given core emphasizes the stability of clay minerals in the marine environment at least over periods of hundreds of thousands of years." Hurley et al. (1959, 1963) found potassium-argon ages of illites from the same area to be on the order of hundreds of millions of years, clearly suggesting a continental source for these clay minerals.

Garrels and Christ (1965, p. 364) suggest on the basis of theoretical studies, ". . . the composition of sea water may be so slightly removed from that required for stability of a great many phases that there is little chemical potential available for equilibration, hence rates of change of unstable species may well be vanishingly low."

The results of many additional investigations are published in which it is clearly demonstrated that the clay-mineral distribution in modern sediments may be explained in terms of source area or segregation of different clay minerals due to size differences and selective flocculation; Biscaye (1964), Griffin (1962), Johns and Grim (1958), Keller (1964), Milne and Earley (1958), Muller (1967), Pryor and Glass (1961), Van Andel and Postma (1954).

Diagenesis Defined

Before citing published evidence for the diagenetic origin of clays, the definition of the term "diagenesis" should be clarified. Gumbel coined the term in 1888 (in Schuchert, 1920, p. 425) and defined it as ". . . the chemical and physical changes that sediments undergo during and after their accumulation, but before consolidation takes place." Recent usage has expanded the definition to include changes taking place after consolidation up to the beginnings of metamorphism, the latter boundary being gradational and therefore controversial. Most current writers approximately follow the definition in the A. G. I. Glossary of Geology and Related Sciences (1960, p. 17 of supplement); "Process involving physical and chemical changes in sediment after deposition that converts it to solid rock, includes compaction, cementation, recrystallization and perhaps replacement as in the development of dolomite." The following writers state some of the varying interpretations of "diagenesis"; Bayly (1968, p. 157), Holmes (1965, p. 92), Krumbein and Sloss (1963, Chap. 7), Mason (1966, p. 248), Pettijohn (1957, p. 648), Read and Watson (1962, p. 255), and Weller (1960, p. 78).

Within the limiting boundaries of depositional and the onset of metamorphism, a number of further subdivisions have been proposed and are discussed in Müller (1967). In the same publication, Müller expands the scope of diagenesis to include preburial physiocochemical processes in both "fresh" water (aquatolysis) and the marine environment (halmyrolysis).

The present writer prefers to limit the definition to the more widely accepted post-deposition usage. An understanding of preburial

processes is, of course, important because most of them are continued or reversed after deposition. Of particular significance are ion exchange "reconstitution" and selective flocculation processes which affect clay minerals upon entering a marine environment. For a further discussion of this aspect, the reader is referred to Fairbridge (1967).

Larsen and Chilingar (1967, p. 524) aptly summarize diagenesis as follows:

> Regardless of how the phenomena may be defined or named, diagenetic transformation may be characterized collectively as the reaction of the sediment or sedimentary rock to its physico-chemical environment. The most important factors here are the pH and Eh of the environment, the concentration of various cations and anions, as well as pressure and temperature.

Support for Diagenetic Origin

Illite

The overall evidence suggests illite is present in all geologic periods but is more abundant in older sediments, particularly those older than Upper Mississippian age. Weaver (1959), among others, explains this variance by non-diagenetic mechanisms. However, the dominance of illite in the older Paleozoic shales is so pronounced that many experienced geologists lean toward diagenesis as being their most probable origin. A change of montmorillonite to illite was first proposed in 1941 by Dietz (in Whitehouse and McCarter, 1958). Grim (1953, 1958) agrees that illite may have formed at the expense of other clay minerals. Even Weaver admits, after a study of Late Cretaceous rocks in Wyoming, that montmorillonite gradually changes to illite via mixed-layer montmorillonite-illite with depth until (1961, p. 154) ". . . at a depth

approximately 10,000 feet no discreet montmorillonite remains." Others have made similar observations in both recent and older sediments; Burst (1959, 1969), Hurley et al. (1960), Murray and Harrison (1957), and Powers (1959). Grim et al. (1949), based on studies of recent sediments, concluded that little montmorillonite was lost during marine diagenesis but instead illite and possibly chlorite form from kaolinite. However, the same writer (Grim and Johns, 1954) later states that montmorillonite in the Mississippi River Delta possibly does alter to illite and chlorite-kaolinite. More recently Grim reports authigenic illite in Sidney Harbor, Australia (Grim and Loughnan, 1962). These examples can all be explained by a reconstitution mechanism. Müller (1967), who has extensively surveyed the literature, believes it is well documented that degraded three-layer minerals take up potassium to form reconstituted illite, and magnesium to form chlorite and chlorite-like minerals. The formation of glacuonite, a dioctahedral ferric illite, is generally accepted as authigenic, and is probably a true "neogenesis" (as opposed to reconstitution), although there is little agreement about the mechanism of formation. Illite that has almost certainly crystallized directly from solution has been identified from several mid-continent sandstones by Rex (1966).

Kaolinite

Kaolinite of unquestioned authigenic origin was reported as early as 1936 by Tarr and Keller, the clay having crystallized from solution in quartz geodes in the Mississippian Warsaw Shale of Iowa. Keller (1967) cites several similar occurrences from the same area and

from southeastern Kansas. Bayliss et al. (1965) report nonhydrothermal dickite from sandstones of the Sidney Basin of Australia. Authigenic kaolinite from deltaic Pennsylvanian sands in southern Illinois has been identified by Potter and Glass (1958). The crystallization of kaolinite from solution has found support in laboratory work with silica and alumina gels by DeKimpe et al. (1961), Murray and Gravenor (1953), and Roy (1954). In a 1963 publication, Fuchtbauer and Goldschmidt conclude that kaolinite commonly forms during shallow burial of argillaceous rocks and is followed below a depth of several hundred meters by a kaolinite-to-chlorite transformation.

Chlorite

Most literature supporting a diagenetic origin for chlorite cites mechanisms involving ion exchange coupled with interlayer brucite precipitation. For instance, Grim and Johns (1954) conclude that detrital calcium-montmorillonite undergoes this process in the Gulf of Mexico, resulting in a montmorillonite--mixed-layer montmorillonite-chlorite--sequence. Powers (1954) cites chlorite of similar origin in the Chesapeake Bay and still more is reported by Pinsak and Murray (1960) in the Gulf of Mexico. Weaver (1959) suggests the sequence volcanic ash--dioctahedral montmorillonite--chlorite. A less severe change is indicated in the work of Murray and Harrison (1957) who found simply an increase in chlorite crystallinity with depth. Biotite as a parent material for chlorite has been reported by Kossouskaya et al. (1965). References to chlorite growing interstitially directly from solution are rare. However, Eckhardt (1958, in Muller, 1967) has found chlorite

chlorite crystals of this type in argillaceous sediments. Blatt (personal communication, 1969) has seen similar chlorite in unmetamorphosed sandstone of the Franciscan Formation (Jurassic) from California. No reports of direct growth of chlorite crystals in the laboratory have been found, although Whitehouse and McCarter (1958) did produce chloritic clay in the laboratory from montmorillonite after a three-year exposure to artificial sea water.

Summary

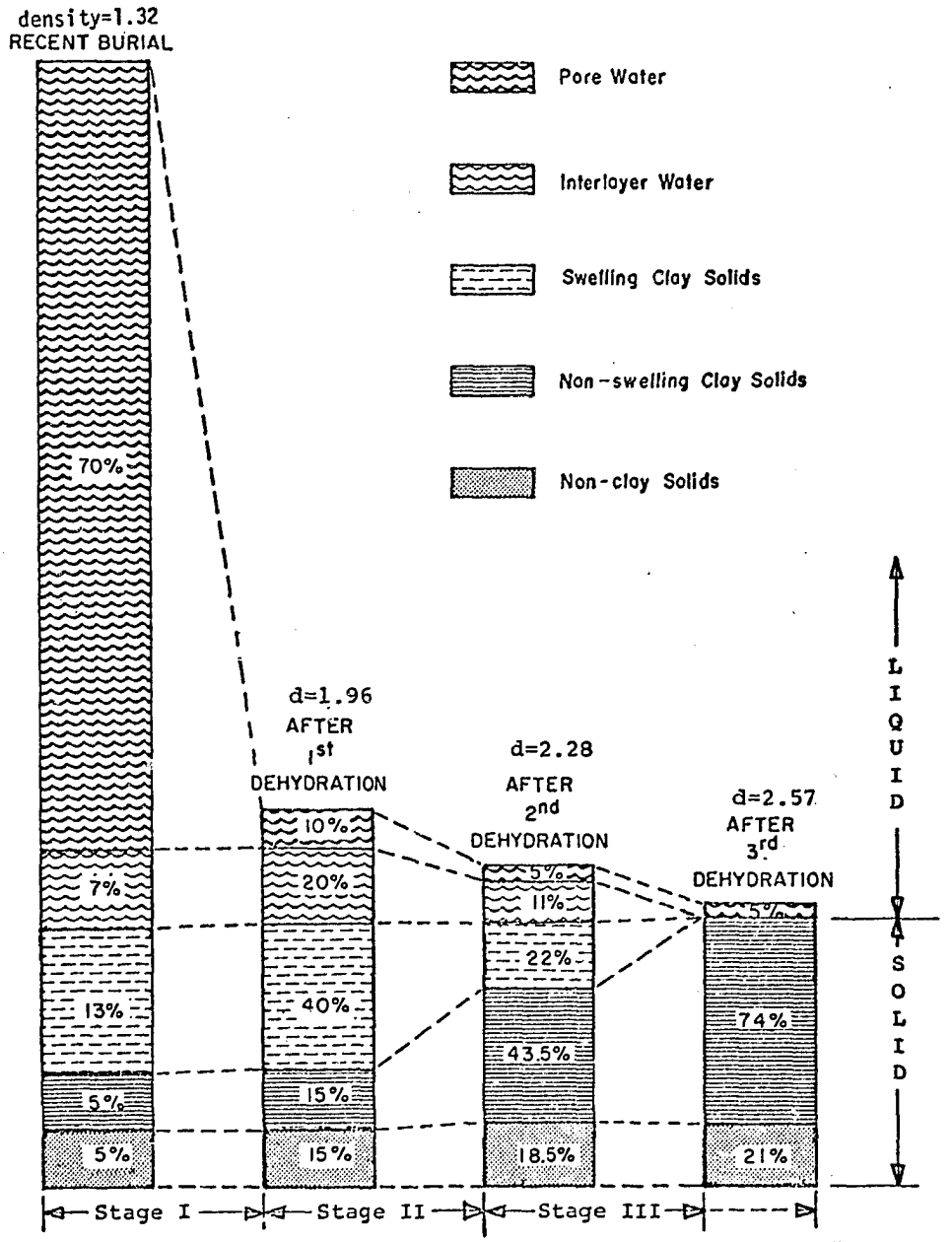
Referring to clay minerals in general, Keller (1967, p. WK-6) does ". . . not hesitate a bit accepting the geologic occurrence of authigenic clay minerals crystallizing from cold aqueous fresh-water solution." For further discussion, the reader is referred to this same publication in which Keller gives an excellent overview of clay mineral occurrence and modes of genesis.

The present writer believes in any discussion of clay-mineral diagenesis, it should be emphasized that two general types of diagenetic mechanisms are involved. The first, and less drastic, may be termed "exchange diagenesis" during which little, if any, change is undergone by the basic crystal structure. This is markedly different from the second, "structural diagenesis," during which an entirely new tetrahedral-octahedral framework may be created.

Most instances cited in support of diagenesis involve only various ion-exchange and hydration-dehydration mechanisms. Degens (1965, p. 39) states: "It should be emphasized that this [geochemical adjustment to environment of deposition] is mainly on an . . . ion exchange

level unaccompanied by marked structural and chemical changes in detrital clay composition." Garrels and Christ (1965) agree that clay minerals are classic examples of solid substances which, when placed with an aqueous solution, show marked tendency to lose certain components while retaining others and gaining still others, all while the basic structure of the original material is preserved.

Many of the "montmorillonite"-to-illite or chlorite alterations are most likely ion-exchange and dehydration phenomena. In 1952, Emery and Rittenberg noted the most important change with depth is water decrease. Burst (1969) presents strong evidence indicating that the numerous reports of montmorillonite altering via mixed-layer montmorillonite-illite phase with depth can be explained by a three-step dehydration mechanism which is largely a function of increasing pressure (overburden) and temperature with depth (see Fig. 1). Stage I involves expulsion of all pore water except a two-layer coordinated water packet between clay sheets, by the action of overburden. Further increase of pressure inhibits the removal of this remaining water. The double interlayer water packet has a higher density than the surrounding pore water, therefore the water tends to expand when expelled into the pores, a process directly opposed by increased overburden pressure. Thus heat energy is needed to assist in the removal of one of the remaining water interlayers in stage II. The final stage III is reached when still additional pressure and heat energy become sufficient to expel the remaining water interlayer. This final stage is slow, even in a geologic sense, probably requiring at least tens of millions of years.



SHALE BULK COMPOSITION DURING DEHYDRATION
(from Burst, 1969, p 81)

Figure 1

Thus a non-expanding illite has been formed from a fully expanding montmorillonite.

Structural diagenesis is also documented, but not nearly as often as the less severe exchange diagenesis. Zen considers physico-chemical relationships among many minerals in sediments and sedimentary rocks stressing the concept of equilibrium among sedimentary mineral assemblages (1959, p. 41); "Existing petrographic evidence is compatible with the hypothesis of equilibrium . . . which carries with it the implication that phase transformations may take place even at near-surface conditions in a reasonably short time. Such transformations include major structural changes of the clay-mineral lattices."

Purpose and Method of Investigation

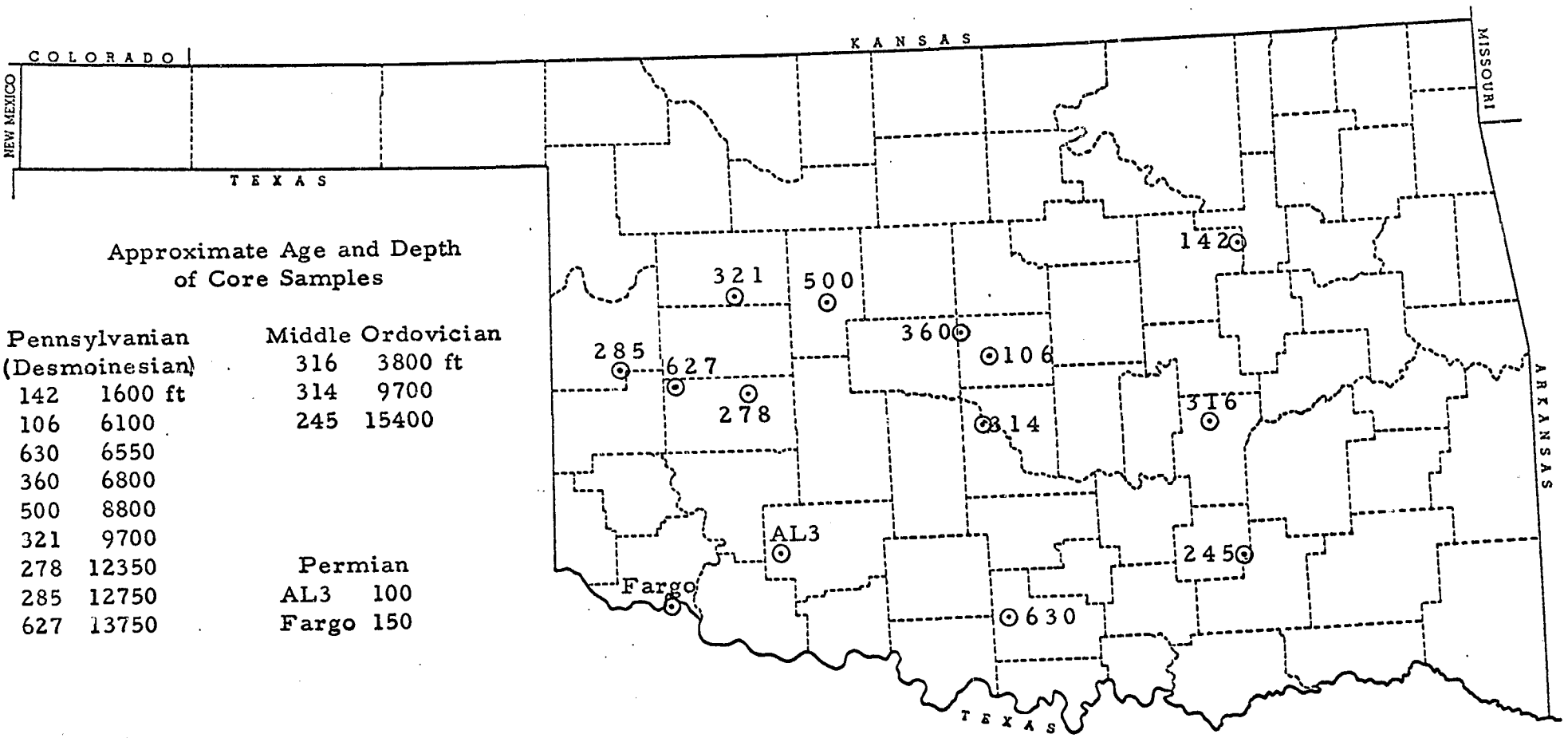
The present study is designed to provide further definitive information in the attempt to ascertain the relative importance of diagenetic and detrital origin of clays in closely associated shales and sandstones. The two lithologic types in the samples chosen were interlaminated with an individual lamina having a thickness on the order of one or two centimeters and frequently as small as one or two millimeters. By limiting the detailed study to such close associations some parameters which could affect clay-mineral content may be assumed essentially invarient. Among these factors which therefore are not determinants of differences of clay-mineral components in the sands and shales studied are pressure (burial depth), temperature, time, tectonics, source rock, general depositional environment, and major climatic variations.

Some major differences do exist, however, which are possible contributors to differences in clay types present in the two lithologies. Particle size variation is the most obvious and most important difference. This, in turn, is controlled by slight differences in energy of transporting media, particularly at the site of deposition. The sorting of detritus in the depositional environment would cause partitioning of mineral types according to size, shape and specific gravity. For instance, among the clay minerals illite commonly occurs in the finest fraction whereas detrital chlorite and kaolinite tend to be larger. Thus it is to be expected when comparing shales and sands that the former should contain a relatively higher percentage of illite. It is also reasonable to expect a higher percentage of non-clay minerals in the sands, thus contributing to an overall difference in bulk chemistry between the sand and shale.

Other important direct results of size differentiation are differences in porosity and, more important, permeability. Initially porosity is higher in argillaceous sediments, being as much as 80 percent in some cases (Müller, 1967). This is reduced rapidly by overburden pressure to approximately 30 percent at a depth of about 150 feet. Krumbein and Sloss (1963) report that most sandstones have porosities less than 30 percent. Thus, at least at shallow depths, shales contain more interstitial water. Migration of this contained water is more important in promoting changes in chemistry than simple static containment. This permeability is strongly affected by grain size, rocks containing larger particles having larger interparticulate connections

and less tortuosity. As a result more fluid migration takes place through sands than shales and sands then have a much greater opportunity to experience intra- and inter-formational transfer of chemical constituents than do shales. On this basis, diagenetic changes are expected to be greater in the coarser sediments.

Samples for study were selected from cores on file at the University of Oklahoma Core and Sample Library in order to eliminate the effect of present-day weathering modifications. The samples were cut from the centers of the cores as a precaution against contamination by drilling fluids and muds. A total of 14 cores from depths of 100 to 15,440 feet and from geographically dispersed locations in Oklahoma (see Fig. 2) were selected for study. From these more than 125 samples were thoroughly examined by various x-ray diffraction techniques, 26 representative thin sections were prepared for detailed petrographic study, and 28 samples were subjected to bulk chemical analysis by x-ray fluorescence. Nine of the cores were from strata of Middle Pennsylvanian (Desmoinesian) age, three from Middle Ordovician rocks, and two from rocks of Permian age. The Desmoinesian samples were subjected to more intensive investigation because they represented the best examples of close shale-sand interlamination. Detailed descriptions of samples and investigation procedures are included in the appropriate appendices.



Approximate Age and Depth of Core Samples

Pennsylvanian (Desmoinesian)		Middle Ordovician	
142	1600 ft	316	3800 ft
106	6100	314	9700
630	6550	245	15400
360	6800		
500	8800		
321	9700		
278	12350	Permian	
285	12750	AL3	100
627	13750	Fargo	150

INDEX MAP OF CORE LOCATIONS

Figure 2

RELATIVE AMOUNTS OF CLAY MINERALS IN SANDS AND SHALES

Procedure

Semiquantitative determinations of amounts of illite, chlorite, and kaolinite were made for 30 shales and 35 sands. The selection of samples studied in this portion of the investigation was governed by the clarity and separation of the (004)-chlorite and (002)-kaolinite peaks at approximately 25° 2θ.

The area under the peak was used as a measure of the intensity of the reflection. This area, in cm^2, was approximated by multiplying the peak height by the peak width at one-half the height. The intensities were then weighted relative to the (001)-kaolinite reflection as suggested by Weaver (1958a) and Murray (1954). When equal amounts of chlorite, illite, and kaolinite are present, their (001)-reflection intensities are 1:1:3, respectively. The intensity of the (001)-kaolinite reflection could not be measured directly due to the superposition of the (002)-chlorite reflection. Therefore the (002)-kaolinite reflection which is about 0.8 as intense as the (001)-kaolinite reflection was measured and adjusted to an (001) equivalence by multiplying by 1.25. The (001) intensities of chlorite and illite were each increased threefold to allow direct comparison among the three clays on each diffractogram.

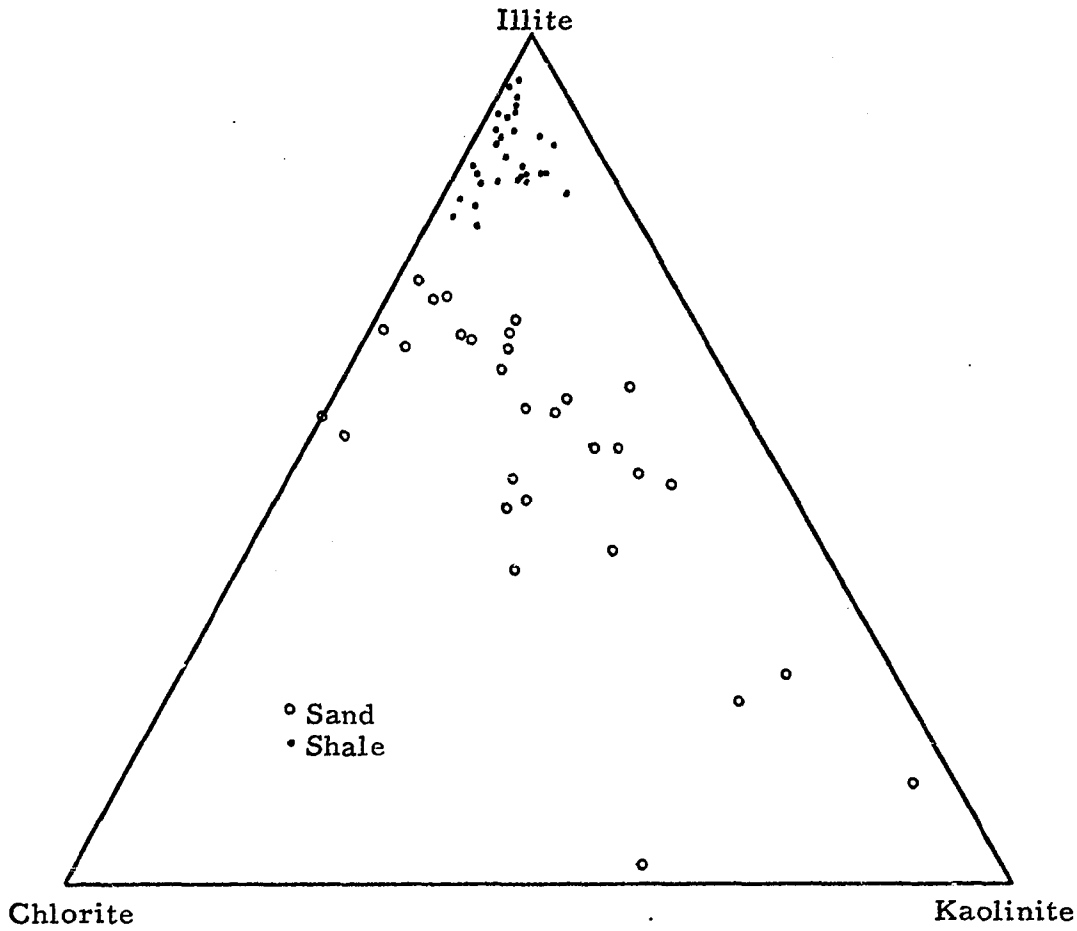
The diffractograms were obtained from both North American Phillips (Norelco) and Siemens-Halske diffraction units at various appropriate scale factors making direct comparisons between diffractograms impossible. An overall comparison was made possible by expressing the amounts of chlorite, illite, and kaolinite as percentages of the total clay fraction in each sample. The results are shown on Fig. 3.

Validity of Semiquantitative Determinations

Sources of Error

Inaccurate measure of actual area. Indistinct peaks were not used. Repeated measurements of the same diffractogram and of subsequent diffractograms of the same sample resulted in close agreement, indicating good precision. The peaks measured closely approximate triangles, any irregularities being smoothed to straight-line averages. Thus the standard mensuration formula for the area of a triangle, $a = \frac{1}{2}bh$, is a valid close approximation. In view of these factors, the measured areas are considered valid.

Inaccurate weighting of measured peak areas. The assumption has been made that the (001)-reflection intensities of chlorite, illite, and kaolinite are 1:1:3, respectively and the intensities of the (002)- and (001)-kaolinite reflections are 0.8:1, respectively. These values are close approximations according to the work of previous investigators (see above). The major objective in this investigation is to determine a semiquantitative comparison between shale clays and sand clays. Because the same procedure has been used in all cases, any consistent differences



RELATIVE CLAY MINERAL CONTENT
OF DESMOINESIAN SANDS AND SHALES
Less Than Four Micron Fraction

Figure 3

are real but not necessarily quantitatively accurate--semiquantitative accuracy is claimed.

Variability of chlorite basal reflection intensities. Intensities of x-ray reflections are related to the atomic scattering factors of ions forming the structure. Ions of similar structure and which are iso-electronic such as Si^{+4}, Al^{+3}, and Mg^{+2} have similar scattering factors. Transition elements of the same period such as Fe, Cr, and Mn also have similar scattering factors, but the factors are about twice that of the first group. In consequence, any substitution of Fe for Mg in the chlorite structure appreciably changes the absolute intensities of the x-ray reflection. In addition, the relative basal intensities are changed (Brindley,1961), as discussed below.

Two important variables to be considered are: (1) the amount of iron in octahedral sites, and (2) the distribution of iron between the "talc" and "brucite" layers. If the iron is equally distributed between the two octahedral locations the intensity of the odd-order reflections is independent of the amount of iron substitution. This is due to the octahedral layer spacing of d(001)/2, resulting in a scattering of waves exactly out of phase for the odd-order reflections, thus making no contribution to these reflections.

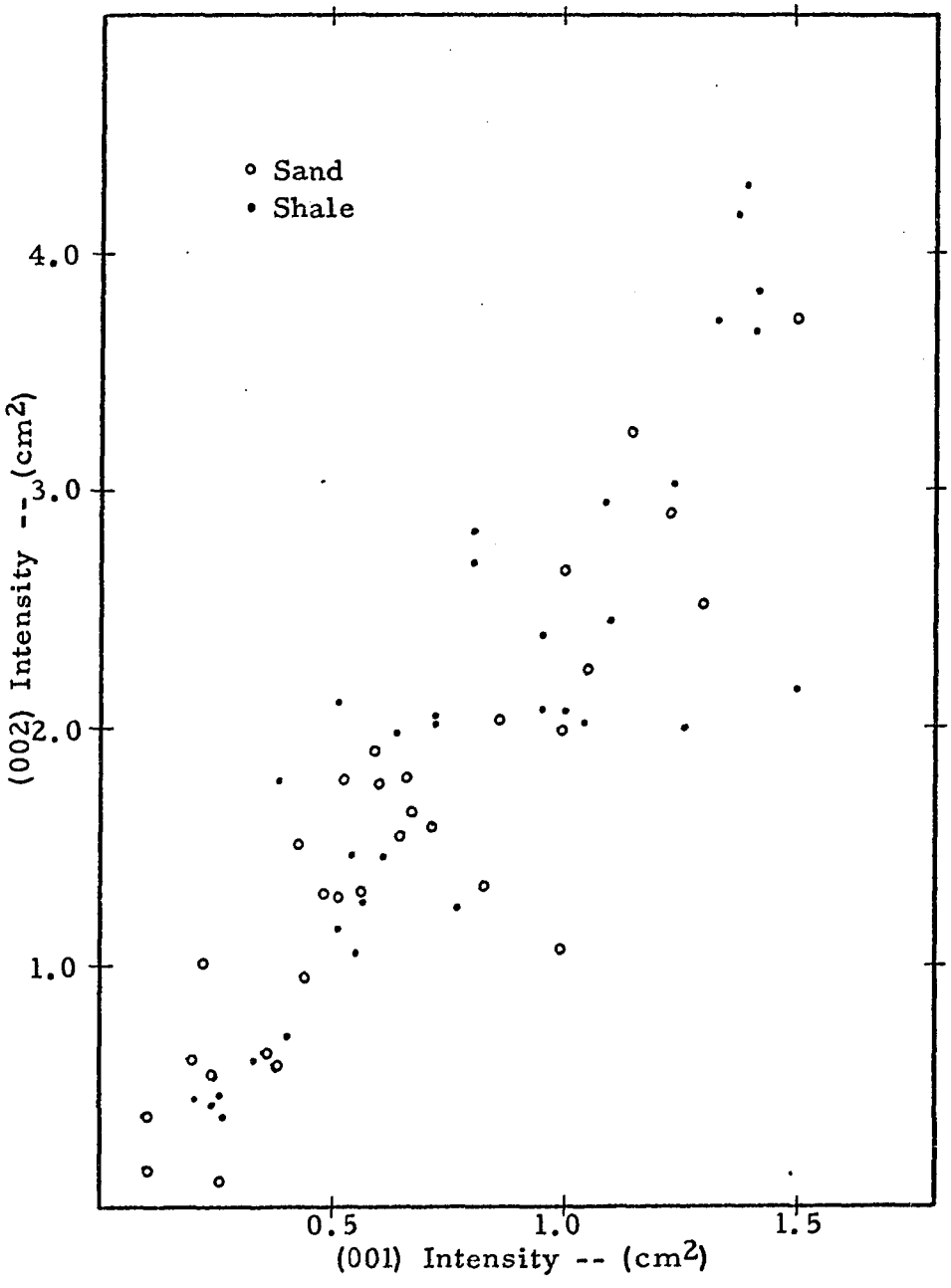
If, however, the iron substitution is not evenly distributed, the result is varying odd-order intensities. For the (001) reflection, the intensity increases (relative to iron-free chlorite) with more iron in the talc layer and decreases with more iron in the brucite layer.

For even-order basal reflections, the two octahedral layers scatter waves that are exactly in phase and therefore the intensity of the (002) reflection is independent of the distribution of iron substitution.

In order to determine if variances in (001) intensities measured in the current investigation are due to varying iron amounts or to actual variations in the amount of chlorite present, a comparison of (002) and (001) intensities was made. If all chlorites are approximately the same, the ratio of these intensities should remain approximately constant in all samples. Figure 4 shows a definite linear trend indicating a constant ratio of (002):(001) intensities thus supporting the validity of assuming variations in (001) intensity are principally due to varying amounts of chlorite. Further support is given by the fact that the variation in iron content of the bulk samples is independent of the (001)-chlorite intensities. From petrographic and x-ray diffraction investigations of the samples, other iron-bearing minerals, notably pyrite, siderite, and various iron oxides, are the iron-determining constituents rather than chlorite.

A problem in determining the (002)-chlorite intensities for the above comparisons was encountered because the (001)-kaolinite reflection is superimposed upon the (002)-chlorite reflection. The following method was devised to surmount this difficulty.

According to Murray (1954), when equal amounts of chlorite and kaolinite are present, the (002)-chlorite intensity is one-half that of the (001)-kaolinite intensity. Thus, with equal amounts of the two clays, one-third of the 7 Å intensity is due to chlorite. For other chlorite-



CHLORITE (002) INTENSITY vs (001) INTENSITY

Figure 4

kaolinite mixtures a proportionate relationship was developed using the following symbolism:

c = portion of 7 Å peak area due to chlorite (002)

k = portion of 7 Å peak area due to kaolinite (001)

T = total area of 7 Å peak

C = actual amount of chlorite

K = actual amount of kaolinite

The relationship is devised by assuming that the variation in (001)-chlorite intensity results only from varying amounts of chlorite. If this is true, the (002)-chlorite intensity, "c", should vary directly with the adjusted (001)-chlorite intensity, "C". If the (001) intensity variation is due to differing amounts of iron, a non-linear plot of (001) vs (002) intensities will result.

The (001) intensity of chlorite is 1/3 as great as the (001) intensity of kaolinite, and the (002) intensity of kaolinite is 0.8 as intense as the (001) intensity of kaolinite:

C = 3 x (001)-chlorite-area

K = 1.25 x (002)-kaolinite-area

The (001)-kaolinite reflection is twice as strong as the (002)-chlorite reflection:

$C \propto 2c$ and $K \propto k$ thus $C/K \propto 2c/k$ or $2c \propto k(C/K)$

If $R = C/K$, then $2c \propto kR$

by definition $k \propto T-c$ and $2c \propto (T-c)R$

thus $c \propto TR/(2+R)$

and finally, since the proportionality factor is constant

$c = TR/2 + R)$.

General Statement

Amounts of illite, chlorite, and kaolinite in Desmoinesian sandstones and shales are compared in Figures 3, 5, 6, and 7. An obvious consistent difference is present between the sands and shales. The shales have a limited range of composition, illite dominating in all cases. Compositional variation is prevalent among sands although illite is still the major constituent in most samples. The percentages plotted are relative to the amount of clay in each sample. As expected, the absolute amount of clay is much higher in the shales than in the sands.

Degraded Clays

The amount of mixed-layer or degraded clay could not be quantitatively measured and is not included in the clay mineral composition as shown in Figures 3, 5, 6, and 7. A semiquantitative estimate of the amount of degraded clay was possible, however, by observing the sharpness of the (001) peaks of illite and chlorite, particularly with respect to the amount of basal broadening of these peaks on the low-angle side as shown on diffractograms of oriented samples. In addition, the amount of shift of this low-angle broadening upon solvation with ethylene glycol was noted. Typical results of this treatment upon a sand-shale pair are illustrated in Appendix C.

Few samples contained appreciable amounts of degraded clays and those that did are not included in the graphical representations. The amount of degraded clay shows a very slight, but inconsistent decrease with depth. The amount of degraded clay varies much more

CLAY MINERAL COMPARISON OF INTERLAMINATED SAND-SHALE PAIRS
(LESS-THAN-4-MICRON FRACTION)

Figure 5

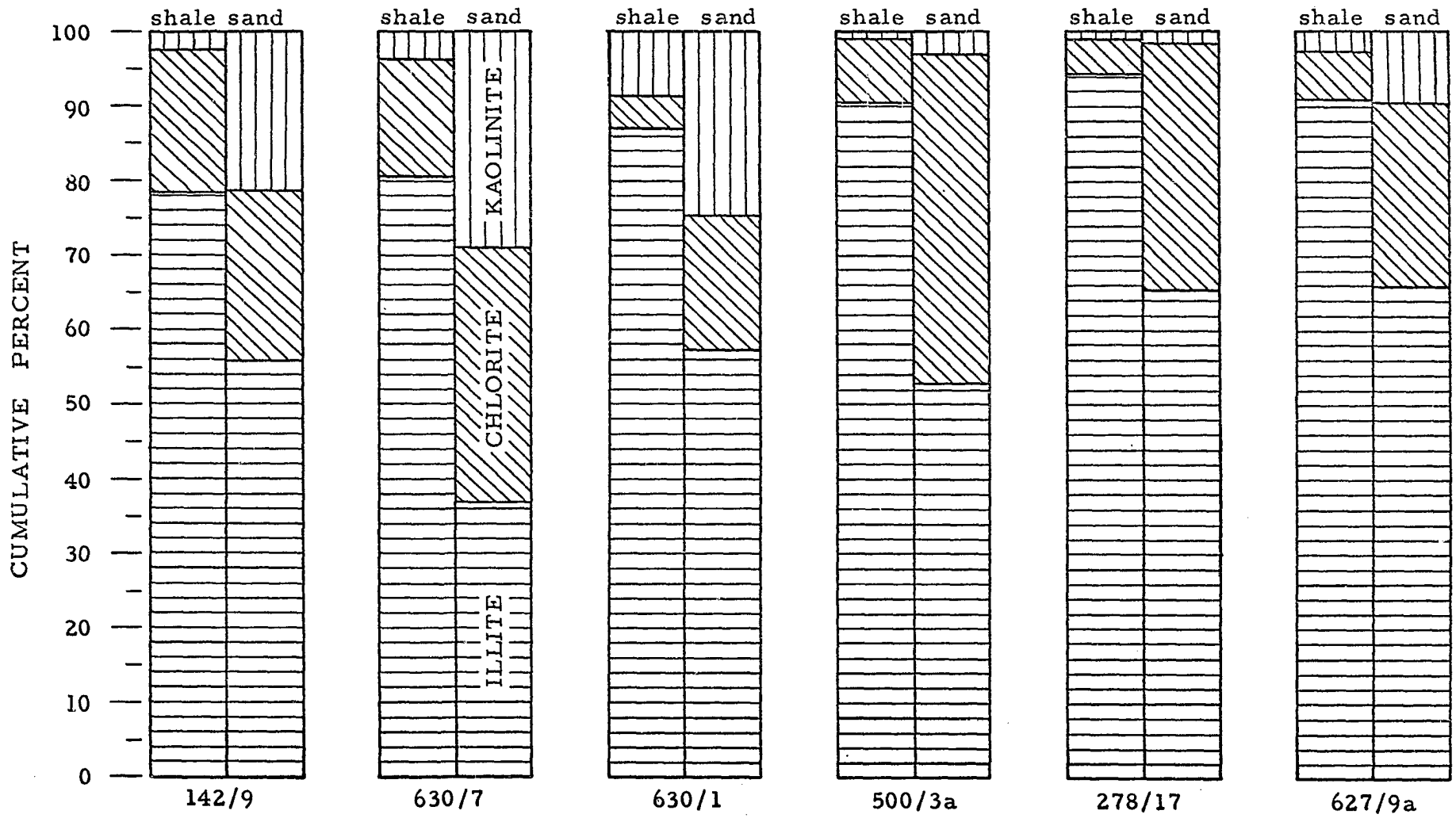


Figure 6

CLAY CONTENT VARIATION WITH SIZE FRACTION

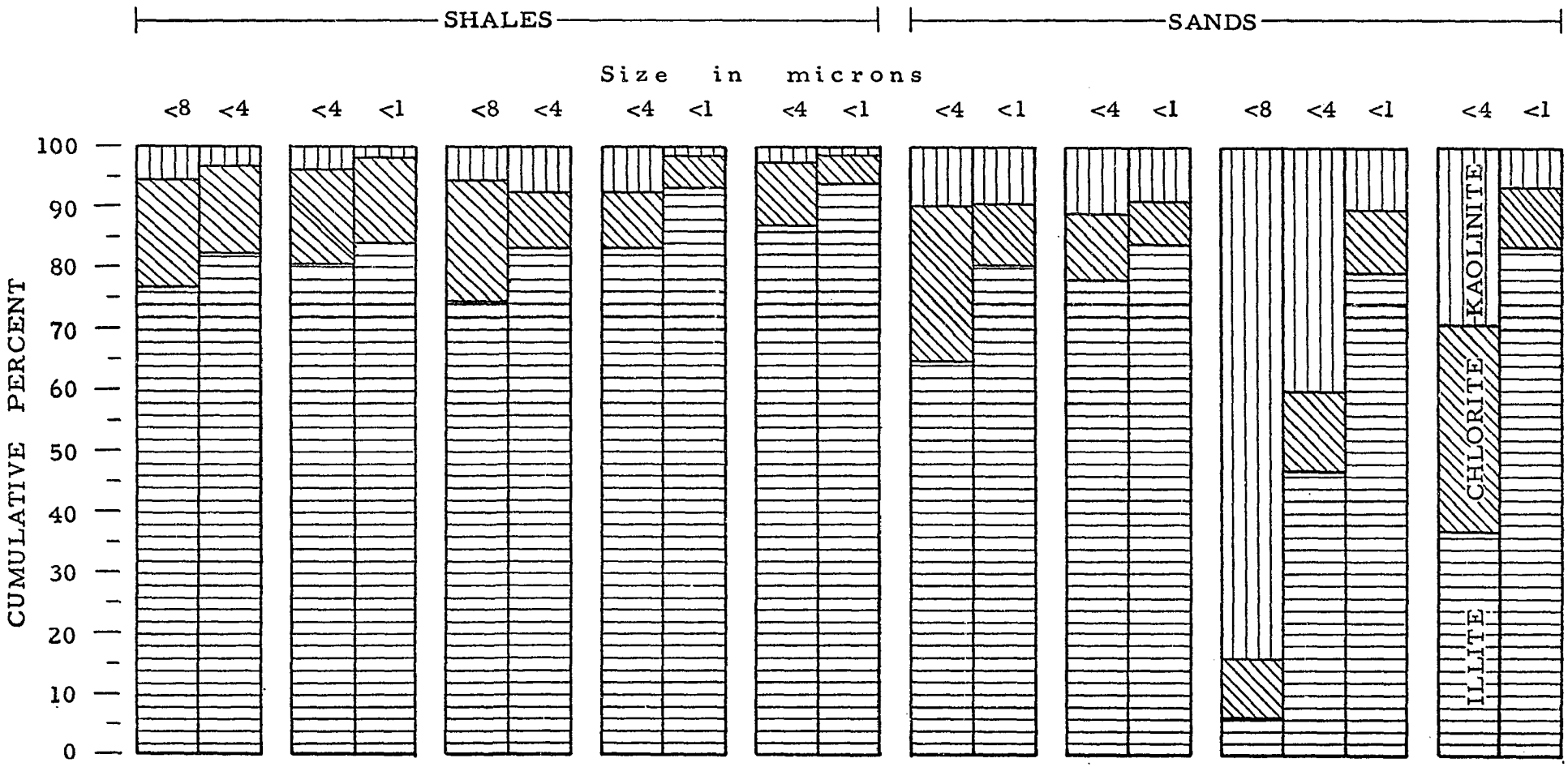
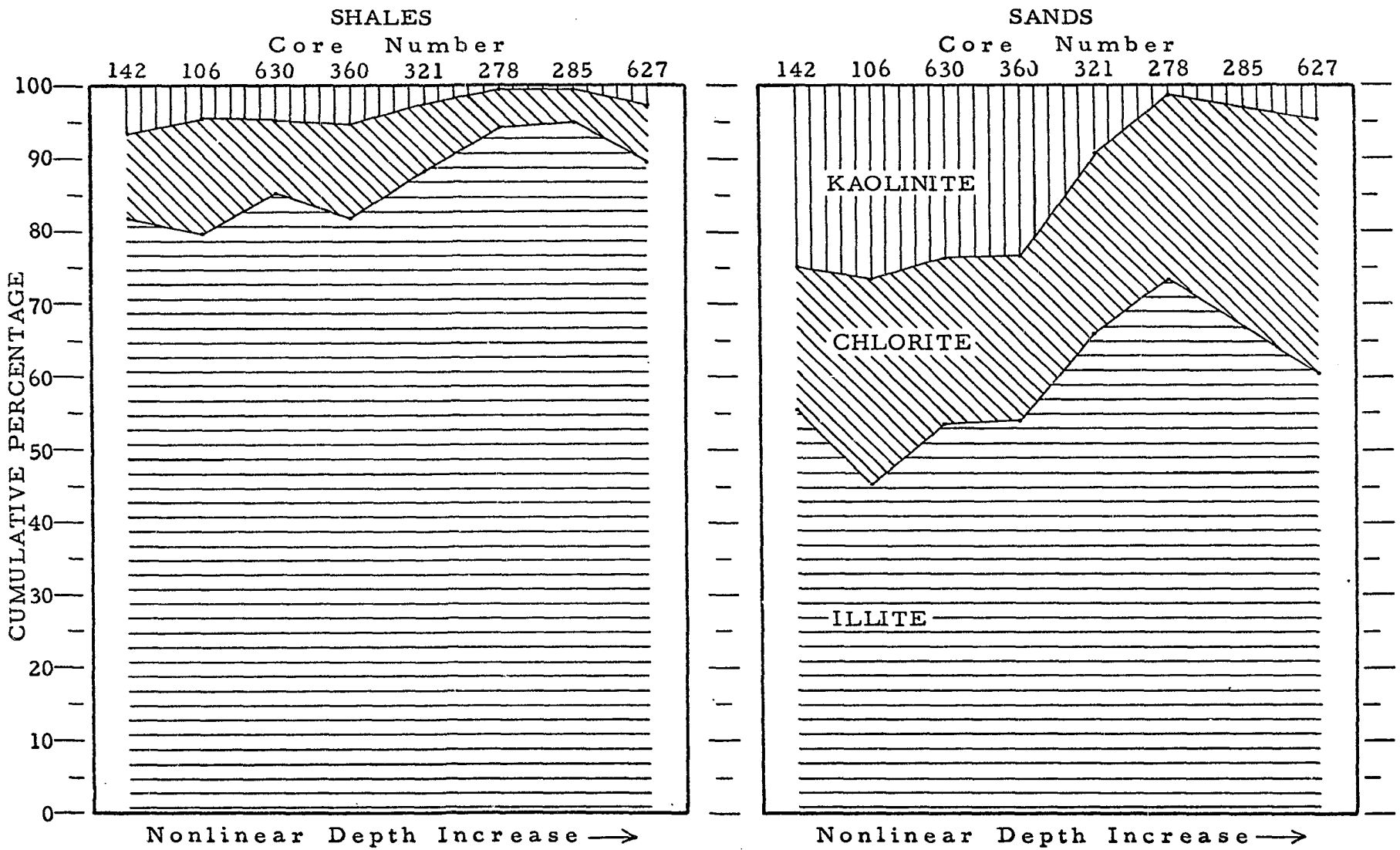


Figure 7

AVERAGE CLAY CONTENT OF DESMOINESIAN CORES



between adjacent sand-shale pairs than between samples taken from different depths. The better crystalline clays are almost invariably associated with sands regardless of the clay mineral in question.

Several inferences can be drawn from these observations. The illite and chlorite were probably brought to the site of deposition in varying states of disrepair imposed by weathering. The great majority of samples studied were deposited in fluvial or deltaic environments and were thus not exposed to high concentrations of dissolved ions. This fresh or brackish water environment severely limited the amount of ion absorption and exchange that took place prior to and during deposition. Those clays deposited as shales or mudstones have been preserved with only minor reconstitution by ion absorption and exchange. Any changes that may have occurred were probably physical changes, notably water expulsion during compaction as described by Burst (1969). Those weathered illites and chlorites deposited in minor amounts along with coarser material were in a post-depositional environment with continued relatively high porosity and permeability even after compaction. These clays had prolonged access to the required ions, notably potassium and magnesium, brought by circulating interstitial water and thereby some weathering effects have been reversed.

Chlorite-Illite

Chlorite and illite are discussed concurrently because they are both interpreted by the writer as being detrital clays. The following evidence is presented in support of this hypothesis.

Illite

As noted above, the clay mineral content of the shales has only limited variability whereas the clay mineral content of the sands shows a relatively broad variation. Although illite is the major constituent in both rock types, it invariably dominates the shale and displays a rather wide variation in relative quantity within the sands. Size fractionation is the most reasonable mechanism controlling this distribution. All samples studied for clay mineral identification were divided into two size groups: less than four microns, and less than one micron. Numerous samples were more extensively fractioned to include sizes from less than eight microns to as fine as less than one-fourth micron. In every case the relative proportion of illite increases with decreasing grain size. Figure 6 illustrates some typical results of this size fractioning. Although relative amounts of clays shown on Figures 5 and 7 are all for less than four micron fractions, there are lesser amounts of illite in the sands than in the finer-grained shales.

The variability of illite amounts in the sands as illustrated in Figure 3 is also related to grain size. The term "sand" is used rather loosely in this investigation and includes mean grain sizes from medium silt through some coarse sand. Most sands are, however, fine to medium. With few exceptions, the coarser sands contain less clay, as expected, but of the clay present, the relative amount of illite becomes less with larger sand size. The general observation that illite tends to be concentrated in finer grain size is not unique, having been noted in previous investigations by this writer and by many other investigators.

Chlorite

The chlorite recorded as clay has been found by thin-section investigation (see Appendix B) to be present both in phyllite rock fragments and as "clay matrix". (The latter is the only form in which illite has been found optically.) This is true particularly in the sand samples because the phyllite fragments constitute part of the sand-size fraction. Figures 6 and 7 show that the major variations in the clay types within the sand samples are accounted for by illite and kaolinite with chlorite variation being relatively small. The illite content varies inversely with increasing sand size as noted above because it is concentrated in the fine clay matrix. The proportion of chlorite remains relatively stable because as the chloritic matrix decreases, the chloritic phyllite increases. The variance in relative amounts of chlorite between sands and shales as shown in Figures 3, 5, and 7 is also largely attributed to the phyllite content of the sands.

Kaolinite

Kaolinite is interpreted as being almost entirely authigenic in origin, probably having formed directly from solution and also by reconstruction diagenesis of some detrital clay material. The major evidence for this comes from thin-section investigations, although x-ray diffraction data supports the idea.

Optically identified kaolinite is always in pore spaces in the form of clusters of granules (see Plate II). The size of the clusters varies and ranges from much smaller to much larger than the average

detrital grain size. This observation by itself suggests the clusters are not detrital. The clusters commonly conform to spaces interstitial to sand grains but do not display any elongation parallel to bedding in those samples where alignment of clay, mica, and organic debris is present. In addition, the boundaries of the kaolinite clusters commonly attack adjacent quartz or potassium feldspars which strongly suggests authigenic growth.

As shown in Figures 5, 6, and 7 the sand intervals consistently have a higher relative kaolinite content than do associated shales. Similar findings have been reported by Glass (1958) and Smoot and Narain (1960) from investigations of Pennsylvanian sediments in Illinois which closely resemble those studied in this investigation. This unequal kaolinite distribution has been attributed by them to the higher permeability of the sands allowing post-depositional kaolinite formation. If the kaolinite is authigenic, it is reasonable to expect that interstitial fluids and their ability to migrate should play an important role in its formation. Weaver (1961, p. 153) states in general: "In recent sediments, kaolinite does not appear to be strongly concentrated in sands rather than muds." Thus the conclusion reached by Glass, Smoot and Narain and independently concurred by this writer gains further support. Confirmation that these clusters are in fact kaolinite is offered by the direct correlation between kaolinite amounts seen optically and recorded by x-ray diffraction analysis.

Thus a combination of optical and x-ray diffraction investigations and comparison with recent sediments strongly suggest that most of the

kaolinite is authigenic whereas illite and chlorite are detrital in origin. The latter two clays have been subjected only to some "repair work" in the sands rather than true authigenic formation.

PROVINANCE AND DEPOSITIONAL ENVIRONMENT

Most of the sands and shales subjected to detailed study during the present investigation are of Desmoinesian age. This age assignment is based upon information supplied by those who donated the cores to the University of Oklahoma (see Appendix A). Although the accuracy of individual unit name identification is open to some question, the Desmoinesian designation is assumed correct. The samples chosen are all similar in megascopic appearance (see Plate I). This writer concludes all the closely interlaminated sands and shales to have delta-associated origins. Sand-shale intervals of striking similarity are found in modern deltaic environments and in ancient units identified as deltaic. The more thickly bedded Desmoinesian sands and shales which were studied are similar petrographically, in clay mineral content and in diagenetic history to the closely interlaminated samples. It is suggested their genesis was not greatly different from the closely interlaminated sequences.

The Pennsylvanian System in Oklahoma is divided into five series which are, in ascending order; Morrowan, Atokan, Desmoinesian, Missourian, and Virgilian. The reader is referred to Branson (1962), Ham and Wilson (1967), Huffman (1959), Tomlinson and McBee (1962), and Visher (1968) for detailed discussions of the overall Pennsylvanian and Desmoinesian

PLATE I

DESMOINESIAN CORE SAMPLES

All samples were photographed in reflected light and are oriented with tops up. The line above each photograph represents one centimeter. These samples closely resemble modern deltaic sediments. Compare with Potter and Glass, 1967, plates 7 and 8, pages 34a and 34b.

A Sample 142/1, Creek Co., depth 1572 ft., X2.

B Sample 142/10, Creek Co., depth 1611 ft., X1.4.

C Sample 500/3b, Blaine Co., depth 8779 ft., X2.

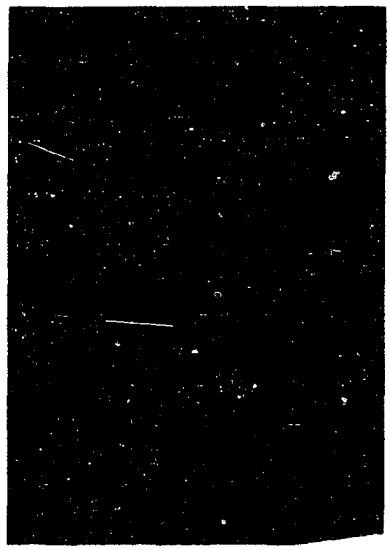
D Sample 321/14, Dewey Co., depth 9725 ft., X0.9.

E Sample 106/4, Oklahoma Co., depth 6096 ft., X 1.4.

F Sample 360/19, Oklahoma Co., depth 6791 ft., X 1.4.

G Sample 630/2, Carter Co., depth 6548 ft., X 2.

PLATE I



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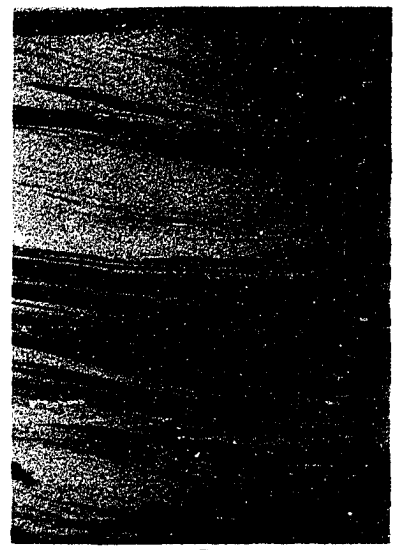

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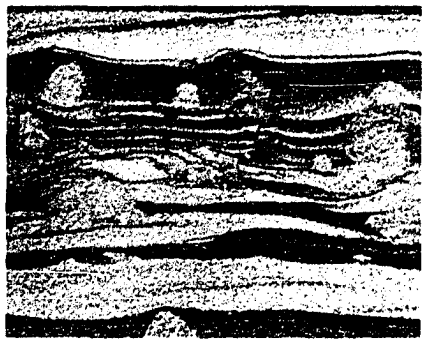

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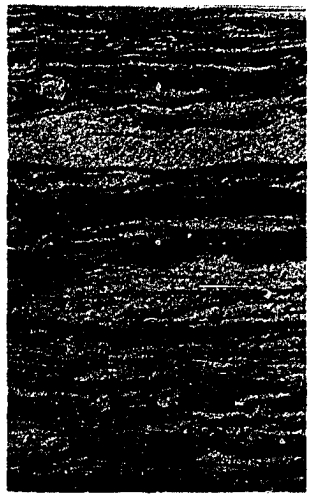

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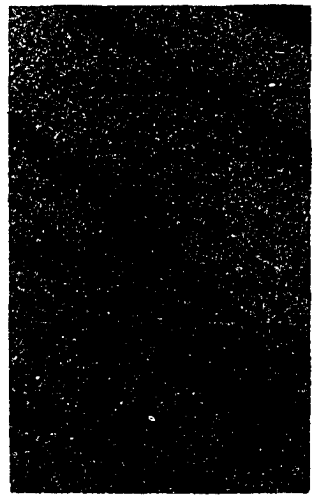

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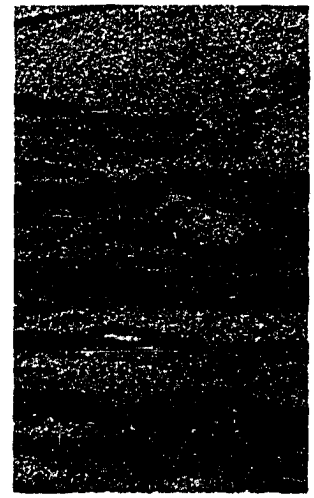
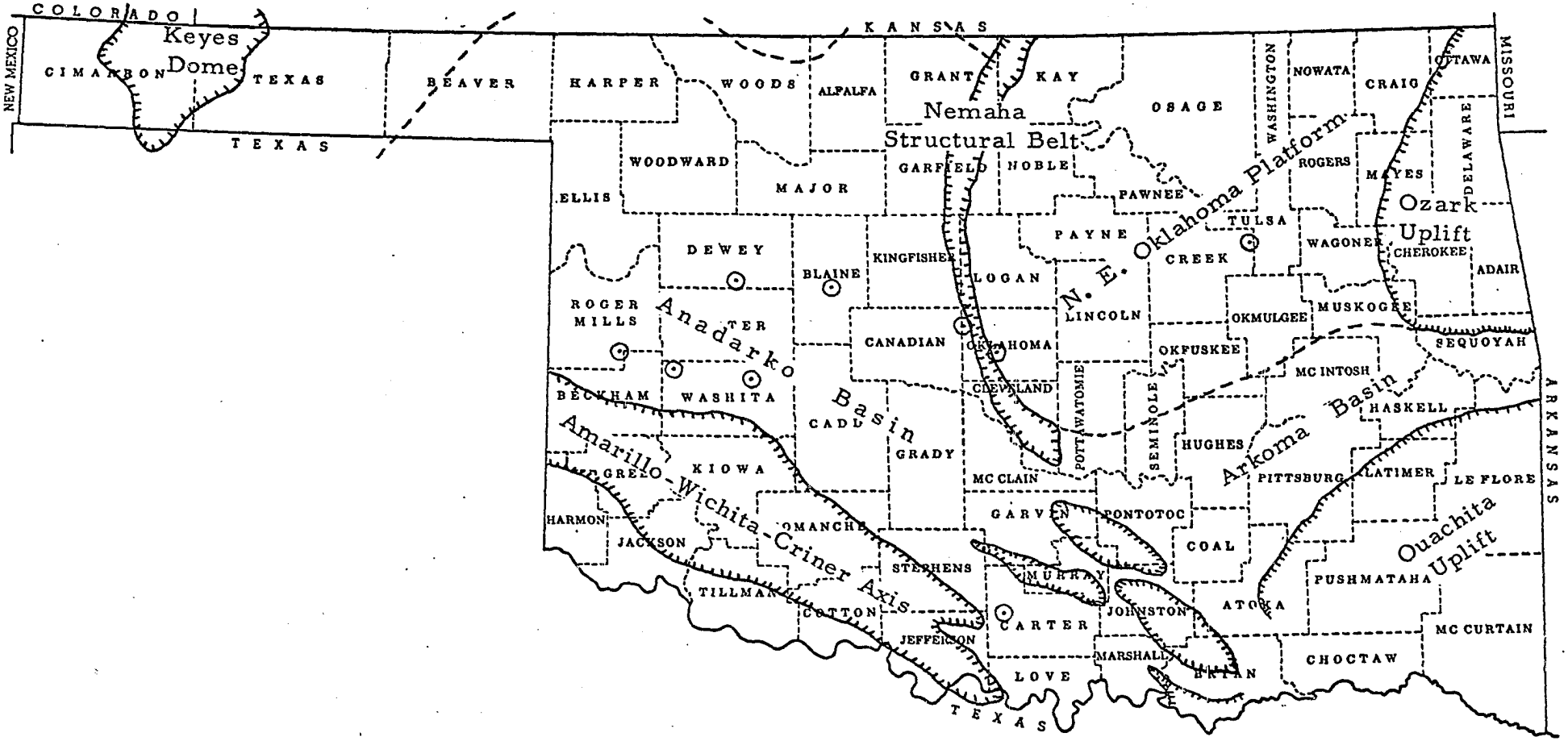


G

sequence of Oklahoma. Figure 8 is a schematic compilation of various structural elements and emergent areas of Oklahoma during Desmoinesian time. As a general description, the Desmoinesian sea spread northward across an eroded and irregular surface causing sediments to be deposited over strata ranging in age from Precambrian to Atokan. The late Desmoinesian sea subsequently withdrew to the south, a widespread regional disconformity resulting after deposition of the overlying Missourian sequence.

In late Morrowan time southern Oklahoma underwent extensive folding and faulting during the Wichita Orogeny (Huffman, 1959). The Ouachita geosyncline was uplifted as were the Amarillo-Wichita-Criner Hills arch, the Nemaha Ridge, and the Hunton-Tishomingo arch. The principal uplift of the Arbuckle Mountains was post-Missourian but earlier movements are indicated (Huffman, 1959). In addition, the Ozark and Central Kansas uplifts experienced renewed epirogenic elevation (Ham and Wilson, 1967). These and other emergent areas supplied sediments from various directions.

Deltas extended northward into the Anadarko basin from the Wichita Mountain area and westward into the basin from the Nemaha Ridge. The latter area was one of only low relief in Desmoinesian time and thus served as an avenue for transportation of sediments from the north rather than as a primary detrital source in itself (G. G. Huffman, personal communication, 1969). Graphic quartz-K-feldspar intergrowths are present within the cores from the Anadarko basin in Roger Mills, Washita, and Dewey Counties. These "micropegmatites" are identical to those found in the Middle-to-Upper Cambrian Wichita and Lugert granites of the Wichita



MAJOR STRUCTURAL FEATURES AND EMERGENT AREAS
IN EARLY DESMOINESIAN TIME
after Branson (1962), Huffman (1959), Jordan and Vosburg (1963), and Tomlinson and McBee (1962).

Figure 8

Mountains (C. L. Merritt, personal communication, 1969) supporting a northward deltaic development. Fragments of polycrystalline quartz and phyllite in these same cores probably originated in members of the Late Precambrian or Early Cambrian Tillman Metasedimentary Group. Volcanic rock fragments, probably from the Late Cambrian Carlton Rhyolite, are also common as are limestone and chert fragments which likely came from Cambro-Ordovician Arbuckle carbonates.

It is interesting to note that graphic intergrowths similar to those mentioned above are present in the core from extreme eastern Creek County, across the Nemaha Structural Belt and 150 miles northeast of the Wichita Mountains. A petrographic study of the Spavinaw granite of Mayes and Delaware Counties, by Merritt (1960), has shown the presence of graphic quartz-K-feldspar in this granite also. In addition, during their study of the basement rocks of the continental interior of the United States, Muehlberger, Denison, and Lidiak (1967) state that micrographic granites are common, if not characteristic, of much of the Precambrian basement through northeastern Oklahoma, southeastern Kansas, and southwestern Missouri. However, essentially all of this basement with the exception of portions of the Nemaha Structural Belt and portions of the Ozark Uplift were covered by pre-Desmoinesian sediments, The source of the Creek County Desmoinesian sediments probably lay to the northeast in the nearby Ozark Uplift. Muehlberger et al. (1967) state that abundant metasediments and rhyolites are associated with the Nemaha and Spavinaw granites in the present subsurface thus accounting for the numerous volcanic and metamorphic rock fragments in this core.

Visher (1968) and Busch (1959) both postulate major Desmoinesian deltaic complexes covering the Northeast Oklahoma Platform. The source area for these distributaries lay to the east and northeast in the Ozark Uplift, to the north in the Central Kansas Uplift, and to the west and northwest in the Nemaha Structural Belt. As stated earlier, the Nemaha Structural Belt was of low relief and not a significant sediment source during Desmoinesian time.

Thus the majority of samples studied during the course of this investigation were deposited in Desmoinesian deltaic complexes with varied igneous, metamorphic, and sedimentary sources in the Wichita Mountains and Ozark Uplift providing the bulk of the detritus.

ORIGIN OF DESMOINESIAN AUTHIGENIC COMPONENTS

Through x-ray identification and petrographic relationships, six authigenic minerals have been identified and the presence of a seventh is implied within the Desmoinesian sands and shales. These include "hydrotroilite," quartz overgrowths, kaolinite, calcite, dolomite, pyrite, and siderite. Each of these is discussed in the following paragraphs in the inferred order of their appearance.

"Hydrotroilite"

The presence of amorphous iron sulfide is suggested by several lines of supporting evidence. By x-ray fluorescence analysis it is clear that the weight percent of both iron and sulfur in the average shale is higher than that of the sands (shale average--5.05% Fe, 3.02% S; sand average--2.65%, Fe, 0.66% S). However, both optical and x-ray diffraction investigations indicate essentially no pyrite in the shales, this mineral being confined to the sands, albeit commonly in small amounts.

The pyrite within the sands is definitely authigenic, invariably being in the form of either individual euhedral crystals or clusters of these crystals. Those who have investigated the formation of authigenic pyrite agree that it is secondary, having been derived from initially-formed hydrotroilite, $FeS \cdot nH_2O$ (Berner, 1964; Degens, 1965; Goldschmidt, 1954; Kaplan et al., 1963). The formation of hydrotroilite is favored by an environment with negative Eh, a probable

condition during essentially the entire post-depositional history of the Desmoinesian sand-shales sequence. This condition is suggested by the abundant carbonaceous remains, especially within the shales. Within the more permeable sands alteration to pyrite was accomplished probably through loss of iron or possibly by the addition of sulfur. The hydrotroilite trapped within the shales has not had access to percolating water and therefore has been unable to achieve the required iron or sulfur transfer.

The initial formation of hydrotroilite probably occurred early in the diagenetic history of the sediments, possibly concurrently with deposition. The sulfur source may have been dissolved sulfates and/or organic sulfur. In any case the availability of sulfur is directly related to bacterial activity (Degens, 1965). Bacteria also tend to concentrate iron within their systems. The initial iron source, however, was most likely various iron-bearing detrital minerals such as chlorite and biotite.

In summary, it is suggested that during or shortly after deposition iron sulfide, as hydrotroilite, was formed within the sediments, particularly the shales with their greater organic content. Later in the diagenetic history, hydrotroilite was altered to pyrite within the more permeable sands, but has remained in essentially its original state within the confines of the shales.

Quartz Overgrowths

Many investigations of solution-precipitation relations of various silica forms have been conducted theoretically and empirically

both in the laboratory and in the field. A few recent references are: Blatt, 1966; Hess, 1966; MacKenzie, 1967; Shcherban, 1967; Siever, 1962; and Swett, 1965.

At 25° C the solubility of amorphous silica is in the range of 100-140 ppm, whereas quartz has a solubility of only 6-14 ppm. The solubility of both forms is independent of Eh and of pH values of less than about 9. Beyond pH = 9.5 the solubility of both quartz and amorphous silica increases sharply reaching about 500 ppm for amorphous silica at approximately pH = 10.5. The same solubility is reached by quartz at about pH = 11.5. Temperature changes also markedly affect silica solubility. Within the temperature range of most diagenesis, 20-200° C, Sievers (1962) using data from numerous investigators finds a solubility increase from 120 to 800 ppm for amorphous silica and from 9 to 270 ppm for quartz.

The silica concentration in soil waters, streams, lakes, and underground waters varies from 5 to 40 ppm with one writer (Livingstone, 1963) suggesting some concentrations as high as 300 ppm. River water commonly is in the interval of 5 to 30 ppm with an overall average value of about 13 ppm. Rivers in tropical areas such as the Amazon have higher averages, those draining temperate areas such as the Mississippi have lower average silica contents. Emery and Rittenberg (1952) have determined a silica concentration of about 40 ppm for pore water.

Early investigators expressed varying opinions concerning the form in which silica is present in water. Although numerous forms are theoretically possible, from colloids to various true solution forms,

the consensus now is that the silica is present as a true solution in the form H_4SiO_4 with ionized forms not being significant until pH values exceed 9 or 9.5. The ionization of H_4SiO_4 at these higher pH values allows the sharp increase in silica solubilities noted above.

Shcherban (1967) states that the overall solubility of silica increases markedly in the presence of dissolved NaCl, dissolved carbonates and "some other salts." These observations are disputed by others however (e.g., Dapples, 1959 and Meents et al., 1952). Better agreement is found with respect to the role of dissolved aluminum ions, the amount of silica in solution decreasing in their presence.

Because the amount of silica in most natural solutions is intermediate between the solubilities of quartz and amorphous silica it is apparent that neither of these species controls the amount of dissolved silica. In the fresh water environment silica is probably supplied through chemical weathering of feldspars and other silicate minerals.

It is clear from these data that the general fresh water conditions are those of supersaturation with respect to quartz and undersaturation with respect to amorphous silica. The standard free energy change for the reaction $H_4SiO_{4_{aq}} \longrightarrow 2H_2O + SiO_{2_{qtz}}$ involves a release of 5.1 kcal/mole of quartz produced (free energy values from Krauskopf, 1967) and, therefore quartz should precipitate from average fresh water. The thermodynamic feasibility, of course, does not reflect kinetics nor does it consider intermediate energy barriers that may be present. These factors apparently do affect quartz precipitation and solubility because neither has been accomplished in the laboratory under normal pH and temperature conditions. Nevertheless given time enough,

quartz should precipitate from interstitial water, and geologic evidence in the form of commonplace quartz overgrowths shows that it does. Dapples (1959) and Siever (1959) both present evidence suggesting quartz overgrowths are characteristic of early burial, being the first diagenetic precipitate--the latter observation is supported in the present investigation. However, syngenetic quartz overgrowths have never been identified in modern sediments (Blatt, personal communication, 1969) thus the definition of "early" burial is open to question.

Quartz overgrowths are common within the Desmoinesian sands although the volumetric percentage is low. None have been observed on quartz grains within the shale intervals. Thin sections in which a diagenetic sequence can be established show quartz overgrowths to be the first-formed authigenic component. The overgrowths commonly have straight euhedral outlines, apparently having grown into pore spaces. Several thin sections clearly contain overgrowths which were present at least before the present state of compaction was accomplished. Clay matrix and phyllite fragments are bent around the overgrowths and in one instance a detrital chlorite flake has been broken by compaction against the sharp euhedral corners of a quartz overgrowth. The sands, being of the arkose-graywacke type have a minimal number of quartz-quartz contacts and therefore interlocking overgrowths do not form a major portion of the cement.

The conditions present at the time of quartz overgrowth formation include a pH less than 9 and a negative Eh environment perpetuated by abundant organic matter. Most quartz overgrowths occurred before compaction was completed; perhaps the expulsion of pore water from

the adjacent shales during compaction provided a continuous replenishment of silica as it was gradually withdrawn by precipitation.

Kaolinite

Evidence has been cited previously (p. 27) supporting the presence of authigenic kaolinite in the Desmoinesian samples studied. Conditions necessary for the formation of kaolinite have been investigated by numerous writers both from geologic occurrences and attempts at laboratory synthesis.

Conditions apparently conducive to kaolinite formation at the surface of the earth are well summarized by Keller (1964). The presence of kaolinite as a weathering product implies: 1) high Al:Si ratio, 2) acid environment, and 3) Na, Ca, K, Mg, Fe absent or "out of circulation." In other words, kaolinite is formed in a climate and terrain where leaching is dominant and low pH conditions prevail, most commonly because of organic activity.

The fact that kaolinite is formed by alteration of aluminum silicates in weathering and diagenetic environments is obvious from geologic relationships, but details of the alteration process(es) remain obscure. Three major paths of formation have been suggested and these are reviewed by Degens (1965). The most basic approach involves interaction between isolated species of monomeric silica and alumina with OH^- and H^+ resulting in the necessary octahedral and tetrahedral units. A second mechanism inserts an intermediate colloidal phase from which crystallization proceeds. The third invokes structural rearrangement of

alumina-silica residue left from selective leaching of parent materials such as feldspars.

Attempts to solve the mechanism problem through laboratory experimentation encounter the usual low-temperature geochemistry pitfall--reaction rates are extremely slow under conditions simulating those found in nature. Although low temperature experiments yield disappointing results with respect to growing kaolinite, these attempts do indicate that aluminum and silicon dissolve separately (Krauskopf, 1967) casting doubt upon the third mechanism listed above. At higher temperatures, leaching reactions are relatively easy to attain in the laboratory. However, the extrapolation back to weathering or diagenetic conditions obviously inserts an element of doubt.

Some promising high-temperature and pressure results have been attained. Hemley and Jones (1964, p. 548) have experimentally determined the stability field for kaolinite for the system $K_2O - Al_2O_3 - SiO_2 - H_2O$ at P_{H_2O} = 1000 atmospheres in a temperature range of approximately 259° C to 500° C. Although extrapolation to low temperature and pressure is tenuous, such a projection of the kaolinite stability field places it within ground and surface water that has been in prolonged contact with feldspar-bearing rocks (Krauskopf, 1967). From thermodynamic considerations, Garrels and Christ (1965, p. 361) have determined the kaolinite stability field in the same system at 25° C and 1 atmosphere. Their conclusion is essentially the same, ". . . most ground and stream waters fall into the kaolinite field of stability." Work by Hess (1966) and Feth, Roberson and Polzer (1964, in Hess, 1966) adds still further conformation.

The empirical and theoretical evidence does not solve the mechanism problem but it does support the geologic findings of the present investigation, and those of others, that authigenic kaolinite does form during diagenesis. Petrographic indications (see Plate II) that kaolinite is replacing or attacking quartz suggests that the Desmoinesian kaolinite is probably precipitated from solution.

It is important to note that the ingredients necessary for formation of authigenic kaolinite in the Desmoinesian sands are present in situ. Feldspars, particularly orthoclase, microcline, and perthite are present as a source for aluminum and silicon and additional silicon can be provided by various other silicates. A key for release of aluminum and silicon by orthoclase is the presence of partly degraded illite which acts as a K^+ acceptor. Investigations of the K_2O-Al_2O_3-SiO_2-H_2O system (Hemley and Jones, 1964) show that a low KCl/HCl mole ratio is necessary for kaolinite to form from K-feldspar, otherwise the formation of authigenic illite is favored. The presence of this mechanism is supported by the anomalous presence of plagioclase in essentially unaltered form as opposed to severely deteriorated K-feldspars. This difference is even noted within perthite where the K-feldspar portions are selectively attacked. Apparently the interstitial water was saturated with Na^+ and Ca^{++} preserving the plagioclase feldspars, but K^+ was being removed by reconstitution of partly degraded illite thus promoting the breakdown of K-feldspars. Further support is offered by the fact that the illites within the sands are commonly better crystallized than their counterparts in the adjacent shales.

PLATE II

SELECTED PHOTOMICROGRAPHS

A. Subarkose: Authigenic kaolinite (center) attacking quartz (left), perthite (below), and metamorphic rock fragments (right and lower left); quartz overgrowths; calcite replacing quartz (left edge) and kaolinite (upper center). Thin section 2133, sample 142/18a, depth 1640 ft., Creek Co., Crossed nicols, X 75.

B. Feldspathic Subgraywacke: Authigenic kaolinite (center) replacing quartz; "pressure solution" contacts between quartz grains, some overgrowths; phyllite grain (bottom) distorted by compaction. Thin section 2127, sample 142/1, depth 1537 ft., Creek Co. Crossed nicols, X 75.

C. Subgraywacke: Authigenic kaolinite (center) replacing quartz on three sides, being replaced by calcite (right); quartz overgrowths; metamorphic rock fragments. Thin section 2123, sample 360/17, depth 6787 ft., Oklahoma Co. Crossed nicols, X 75.

D. Argillaceous Subarkose: Fresh plagioclase (center) attacked by calcite; limestone fragment (top); quartz overgrowths (upper right); composite quartz (lower center); siderite grains throughout. Thin section 2341, sample 285/104, depth 12754 ft., Roger Mills Co. Crossed nicols, X 75.

E. Feldspathic Subgraywacke: "Diapiric" intrusion of silt into shale lamina. Thin section 2342, sample 500/3b, depth 8779 ft., Blaine Co., Open nicols, X 15.

F. Arkose: Quartz overgrowth (top center); several varieties of graphic intergrowths of quartz and feldspar. Thin section 2343, sample 278/19, depth 12349 ft., Washita Co. Crossed nicols, X 75.

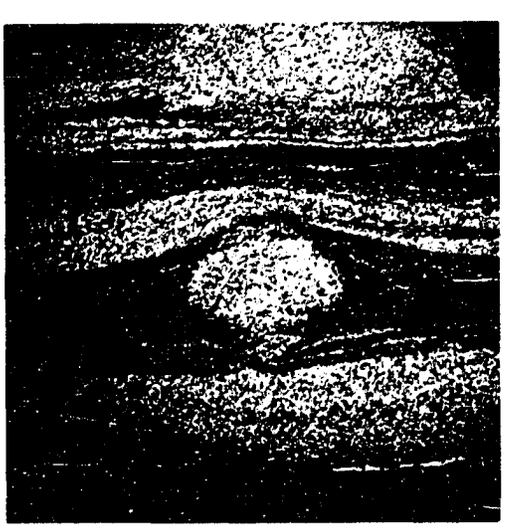
PLATE II

A

B

C

D



E

F

In summary, the formation of authigenic kaolinite in the Desmoinesian sands was possible by the interplay of four major factors;

1) porosity and permeability allowing migration of interstitial water,
2) presence of K-feldspars as a source of Al and Si,
3) presence of partly degraded illite as a K^+ acceptor,
4) presence of organic material to maintain a low pH.

Authigenic kaolinite is not present in Desmoinesian shales because factors 1 and 2 are severely limited.

Authigenic kaolinite is not present in the Ordovician orthoquartzites investigated because factors 2 and 4 are absent.

Authigenic kaolinite is not present in the Permian "granite wash" investigated because factors 3 and 4 are absent.

Calcite and Dolomite

Calcite and, to a lesser extent, dolomite have been introduced in varying amounts as authigenic cement. In all instances where the diagenetic sequence could be determined, the carbonate cement definitely postdates quartz overgrowths and authigenic kaolinite. This diagenetic order is commonly reported in the literature: Dapples, 1959; Krauskopf, 1964; Potter and Glass, 1958; Siever, 1959; Sujkowski, 1958; and Von Englehardt, 1967. In the Desmoinesian sands of the present study the carbonate cement is rarely present as a passive pore filling, rather it is replacing all detrital grains to varying extents and also is replacing authigenic kaolinite.

The conditions and mechanisms necessary for precipitation of calcite in this environment are frequently discussed but as yet no firm answers are available. Of course, a single answer cannot be found for all sediments due to to the wide variety of parameters involved. However, some general lines of evidence are being uncovered. The precipitation of calcite cement in the pores of sandstone depends largely upon increasing the $[Ca^{++}][CO_3^{=}]$ product in interstitial waters. The most obvious way to accomplish this is to raise the pH of the environment. The common antipathetic relationship between quartz and calcite has been attributed by Correns (1950) to the inverse relationship of their solubulities with increasing pH. As stated earlier, the solubility of quartz is virtually independent of pH for values less than about 9. Although values this high have been shown theoretically possible and have been produced in the laboratory under diagenetic conditions (Garrels, 1960; Krauskopf, 1967), the circumstances necessary are rather unique. Siever (1962), among others therefore suggests that temperature increase with depth likely plays a more important role in the precipitation of calcite and concurrent dissolution of silica. Miller (1962) has demonstrated the decrease in calcite solubility with increasing temperature in a closed system with constant P_{CO_2}. Similar results should occur in an open system because increasing temperature decreases the solubility of CO_2 thereby encouraging calcite precipitation.

Increasing temperature with increasing depth is accompanied by increasing pressure. Higher pressure favors dissolution of both quartz and calcite, but Degens (1965) indicates the solubilities of the two

increase at about the same rate and effects of temperature increase overshadow those of pressure increase.

The temperature effect lessens the amount of pH variation needed but does not eliminate the necessity of some pH increase. The change in conditions from at least weakly acid during early diagenesis to basic during carbonate precipitation must still be accounted for. A simple answer is to call on percolating waters to come from lower temperature environments and precipitate the carbonate cement in the sands in question. These solutions could themselves bring a pH rise. An essentially in situ mechanism could also be operative. Natural chromatography has been demonstrated by Bredehoeft et al. (1963), Chave (1960), and Nagy (1960) to effectively increase the ion concentration in the sands. The interlaminated shales act as physical and chemical filters allowing water molecules to pass through but stopping most dissolved ions at the sand-shale interface. Von Englehardt and Giada (1963) have demonstrated that an additional mechanism is operative between interlaminated sands and shales. As water is mechanically squeezed from the shales, the solution left behind in the shales is less concentrated than that expelled into the sands. Thus the passage of water both into and out of sands tends to increase the ion concentration in the sands.

Any or all of these processes could have played a role in the development of the calcite cement in the Desmoinesian sands. There is a general, although inconsistent, tendency for the sands from greater depths to contain more calcite suggesting that the temperature effect may have played a significant role. In any case it is clear that the

precipitation of calcite followed the formation of kaolinite and thus at least a minor effective increase in pH occurred.

Dolomite precipitation requires conditions similar to those needed for calcite precipitation, and as with calcium ions, magnesium ions are probably present in adequate supply for dolomite formation (Blatt, 1966). However the highly ordered placement of calcium and magnesium ions within the dolomite structure causes a lower nucleation rate than that of calcite. Although it is not petrographically clear that calcite precipitation preceded that of dolomite in the Desmoinesian sands, this order is probable.

Pyrite and Siderite

The latest diagenetic products, as shown by petrographic relationships, are pyrite and siderite. Most authors who discuss the diagenetic formation of pyrite agree that the initial form is hydrotroilite, $FeS \cdot nH_2O$. Alteration of hydrotroilite to FeS_2 can lead to either of the dimorphs, pyrite or marcasite, depending to a major extent upon the pH of the environment (Degens, 1965), pyrite formation being favored by alkaline and marcasite by acid environments. In order to accomplish this change there must be a relative enrichment in sulfur. This can be accomplished either by loss of iron or gain of sulfur, both mechanisms having been suggested. Kaplan et al. (1963) suggests addition of sulfur whereas Goldschmidt (1954) supports the loss of iron.

The writer suggests the following sequence for pyrite formation in Desmoinesian samples. Early in the diagenetic history, perhaps concurrent with deposition, hydrotroilite was formed. Bacterial decay of

organic matter was the major sulfur source while iron came from iron-bearing detrital minerals. The hydrotroilite remained in this form until conditions developed favoring the precipitation of calcite cement. These alkaline conditions favored the formation of pyrite rather than marcasite and allowed removal of iron which subsequently was incorporated with carbonate to form siderite.

Evidence supporting this sequence of events includes the close association of calcite, siderite, and pyrite, the pyrite being preferentially associated with organic debris. Lesser amounts of either calcite or organic remains corresponds with less pyrite, and pyrite is never found without associated siderite. The pyrite is present almost exclusively within the sands indicating the presence of interstitial water played an important role in its formation. The dark color invariably associated with the shales may be due in part to remaining hydrotroilite. From thermodynamic considerations, the formation of pyrite and siderite from hydrotroilite and dissolved carbonate is favored by a standard free energy release of 49.8 kcal for the reaction:

$FeS + CO_3^{=} \longrightarrow FeS_2 + FeCO_3$ (Standard free energy values from Krauskopf, 1967).

Formation of quartz overgrowths and authigenic kaolinite is seen petrographically to have preceded calcite introduction and siderite postdates calcite. Early diagenetic conditions were acid, kaolinite having an abrasion pH of 5 to 7 (Degens, 1965). If transformation of hydrotroilite were to have occurred during this phase of diagenesis, marcasite would have formed. None has been identified optically nor through x-ray investigation and the pyrite is invariably euhedral,

commonly as octahedra or cubes with no indication of pseudomorphic replacement of orthohombic marcasite. Thus an overall trend toward higher pH conditions during diagenesis is suggested.

CHEMICAL ANALYSES

Twenty-eight samples were chemically analyzed by x-ray fluorescence. Of these, five were from Permian strata, three from Ordovician strata, and the remaining twenty were from ten sand-shale pairs from Desmoinesian strata. The analyses of nine samples have been rejected because of questionable total percentages. Most of these rejected analyses indicated unusually high amounts of carbonate (calcite, dolomite, siderite) and/or high amounts of sulfur. The totals for these samples were well over 100 percent due to an appreciable difference in matrix effect between the samples and the standards used causing less fluorescence radiation to be absorbed in these samples than in the standards.

Because monomineralic separations were impossible, analyses were necessarily made of bulk sand and shale samples resulting in data of limited value to the present study. Several items of interest can nevertheless be extracted.

Expected differences between the sands and shales are evident. The average SiO_2 content of the sands is higher than that of the shales (73.35% vs 55.50%) reflecting the higher quartz content of the sands. Average Al_2O_3, MgO, and K_2O amounts are higher in the shales because of more clay in these samples (Al_2O_3, 21.13% vs 9.42%; MgO, 2.65% vs 1.57%; K_2O, 4.06% vs 1.32%). The higher weight loss by the shales upon ignition

(7.20% vs 3.88%) is attributable to their same higher clay content and the concomitant combined water.

Other differences in average composition occur in FeO, TiO_2 and S, all of which are present in more abundance within the shales (FeO, 6.67% vs 3.98%; TiO_2, 1.19% vs 0.68%; S, 1.53% vs 0.26%). These differences, particularly in iron and titanium, probably indicate a higher percentage of heavy minerals within the shales. The relative scarcity of these minerals in the sands may be a function of higher porosity and permeability in the coarser sediments allowing them to be selectively leached from the sands. The higher sulfur content of the shales is accounted for, at least in part, by their higher organic content. Higher CaO within the sands (3.89% vs 1.07%) is almost certainly due to the selective introduction of calcite cement into the more permeable sands.

In general, the lack of major unexpected differences in bulk chemical composition between the Desmoinesian sands and shales supports the hypothesis that authigenic mineral formation is quantitatively unimportant.

Refer to Appendix C for tabulation of analyses and procedural details.

CONCLUSIONS

Diagenesis, especially with reference to clay minerals, should be viewed at two levels of "intensity." The first involves a relatively simple rebuilding or reconstitution process by ion exchange, the basic structural framework of the mineral remaining intact. The presence of this process within the Desmoinesian samples is evident on x-ray diffaction patterns. Comparison of the amount of degraded character of illite and chlorite in sand-shale pairs almost always shows better crystallinity in the sands and never better crystallinity in the shales. The reasonable conclusion is the clays in the shales more nearly represent the condition of the clays as they were supplied to the depositional site, whereas those in the sands have undergone more reconstitution diagenesis.

True authigenic mineral formation is quantitatively unimportant with the possible exception in a few instances of abundant carbonate cements in sands. Chemical analyses show little compositional variance between sands and shales other than those associated with expected detrital differences.

Permeability and porosity are the basic factors controlling the amount of diagenesis that occurs. Coarser-grained sediments naturally have more water-filled pore space after compaction allowing the aqueous chemistry of diagenesis to proceed. Authigenic mineralization such as quartz overgrowths, kaolinite clusters, and pyrite crystals are present

in sands up to the shale-sand interface, but apparently are essentially absent in the shales.

The distribution of illite, chlorite, and kaolinite between the Desmoinesian sand-shale pairs is a function of several factors. Illite is the dominant clay in all shales and most sands reflecting the mineralogy of the source area, however it is relatively more abundant in the shales and in the finer size fractions of both sands and shales. Thus, its distribution is controlled by fine grain size. Chlorite distribution is variable, not being directly related to grain size, because this mineral is present both as clay and in the silt-sand-size fraction as metamorphic rock fragments. Kaolinite is a much more important constituent in the sands for diagenetic reasons listed below and is present in decreasing amounts in finer size fractions because of the large (for clay) size of the authigenic kaolinite crystals and aggregates.

Authigenic kaolinite formation was possible because four coexisting factors were present: organic material to help maintain a low pH through bacterial activity, potassium feldspars as a source of aluminum and silicon, partly degraded illite as an efficient "sink" for potassium released during feldspar decomposition, and water-filled pore space allowing aqueous solution chemistry to proceed and to provide growth space for the kaolinite. Authigenic kaolinite is absent or nearly so in Desmoinesian shales, Ordovician orthoquartzites, and Permian shales and arkoses because one or more of these four factors was absent. The formation of authigenic kaolinite in the Desmoinesian sands did not require long-distance transport of necessary ions, all ingredients being present in situ.

The sequence of authigenic mineral formation as observed in thin section is: quartz overgrowths, kaolinite, calcite, dolomite, and finally pyrite-siderite. An additional initial authigenic mineral, "hydrotroilite," is proposed.

Negative Eh conditions, at least in the macroenvironment, were present throughout the diagenetic history as attested by abundant carbonaceous organic remains. There was a general trend toward a higher effective pH as diagenesis progressed. The actual change in pH may have been minor because increasing temperature (increasing burial depth) has much the same effect on solubilities, especially of quartz and calcite, as an increase in pH.

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APPENDICES

APPENDIX A

SAMPLE DESCRIPTIONS

Desmoinesian, Ordovician, and/or Permian stratigraphic intervals of 36 core were examined. Fourteen of these were investigated in detail. Representative samples of lithologic variations were selected for further laboratory study. These representative samples are herein described.

Accession numbers are those by which the cores are cataloged in the University of Oklahoma Core and Sample Library. Sample numbers correspond with box numbers from which the samples were taken. For example, sample 245/3 was taken from box 3 of the core with accession number 245. Identification of the units is based on information supplied by the operators. Colors have been assigned by comparison with the G. S. A. Rock-Color Chart.

Acc. no.: 106. Location; SW-SE, sec. 17, T13N, R3W, Oklahoma Co. Operator: Gulf Oil Co., #1 Jesse, 4 in. core. Sample depths: 6089-6098 ft., Desmoinesian (Bartlesville), 6663 ft., Ordovocian (Simpson).

Sample Number	Depth (ft.)	
1	6087	Shale, brownish black (5 YR 2/1), silty, well indurated, subparallel parting along bedding, fine (< 1 mm.) lenses of medium light gray (N 6) silt account for 5% of sample.
2	6089	Shale and silt, similar to sample 1, silt accounts for 50% of sample, disrupted bedding.
4	6094	Shale and silt, similar to sample 2, bedding more regular, "diapiric intrusions" of silt into shale.
6	6098	Silt and shale, similar to sample 4, silt accounts for 75% of sample.
9	6663	Silt, light olive gray (5 Y 7/1), calcareous, uniform, some diffuse irregular thin (0.5 mm.) red brown stringers.

Acc. no.: 142 (new no. 942). Location; SE-SW-NE, Sec. 29, T18N, R12E Creek Co. Operator: Gulf Oil Corp., #2-C-9W, 4 in core. Sample depths: 1572-1652 ft., Desmoinesian (Glenn Sand of Bartlesville).

Sample Number	Depth (ft.)	
1	1572	Sand, uniform light gray (N 7) with irregular clay laminae, light olive gray (5Y 6/1), thin section 2127.
2	1573	Sand, similar to sample 1, numerous randomly spaced carbonaceous flecks.
3	1583	Sand, uniform greenish gray (5 GY 6/1), well indurated.
6	1594	Sand, uniform light olive gray (5 Y 6/1), well indurated, thin section 2128.
8	1605	Sand, uniform light brownish gray (5 YR 6/1), fine black laminae.
9	1608	Sand, uniform light olive gray (5 Y 6/1), fine black laminae, thin section 2129.
10	1611	Sand, similar to sample 9, small-scale disrupted cross bedding, slumping, channeling.
14	1622	Sand, dark medium gray (N 4), well indurated, grades rapidly to claystone, pale yellowish brown (10 YR 6/2), silty, sideritic, well indurated.
15a	1623	Calcarenite, dark greenish gray (5 GY 4/1), fossiliferous.
15b	1624	Calcarenite, similar to sample 15a, irregular diffuse black areas, thin section 2131.
15c	1625	Shale, greenish black (5 G 2/1), well indurated, fissile, sharp contact with overlying calcarenite, thin section 2131.
16	1631	Shale, similar to sample 15c, less fissile.
17	1637	Sandstone, light olive gray (5 Y 6/1), dark micaceous films.

Acc. no.: 142 (new no. 942)--Continued.

Sample Number	Depth (ft.)	
18a	1640	Sandstone, light olive gray (5 Y 6/1) to light brownish gray (5 YR 6/1), gray portion contains well crystalline kaolinite (x-ray), brownish portion is sideritic, thin section 2133
18b	1641	Sandstone, light gray (N 7), friable, dark carbonaceous flecks.
18c	1642	Shale, dark gray (N 3), well indurated, fissile.
19a	1643	Shale, similar to sample 18c.
19b	1644	Mudstone, greenish black (5 G 2/1), shiny, not fissile, coaly, thin section 2132.
19c	1644½	Mudstone, similar to 19b, contains hard siderite concretion, pale yellowish brown (10 YR 6/2), 2 in. diameter, thin section 2344.
20	1645	Siltstone, light gray (N 7), numerous fine irregular coaly veinlets.
21a	1649	Siltstone, similar to sample 20, additional shaly laminae.
21b	1652	Siltstone, similar to sample 21a, shale, dark gray (N 3) accounts for 50% of sample, thin section 2130.

Acc. No.: 245. Location: C-SE-SW, Sec. 26, T1N, R11E, Coal Co.
Operator: Pasotex Petroleum Co., #1-A Underhill Unit, 4 in. core.
Sample Depths: 15429-15447 ft., Ordovician (Simpson).

Sample Number	Depth (ft.)	
1a	15429	Shale, medium dark gray (N 4), well indurated, no bedding visible, irregular fracture, minor fossil debris, irregular calcareous blotches, light gray (N 7).
1b	15431	Limestone, dark greenish gray (5 G 4/1), abundant fossil debris, coarsely crystalline, subparallel alignment of fossil fragments,
1c	15433	Shale, brownish black (5 YR 2/1), shiny, irregular bedding and parting, calcareous intraclasts, thin section 2126.
2a	15434	Shale, similar to sample 1c.
2b	15436	Limestone and shale, limestone as in 1b with dull medium dark gray (N 4) shale irregularly interspersed accounting for 20% of sample.
2c	15440	Shale, medium dark gray (N 4), dull, irregular parting, uniform, well indurated, thin section 2125.
3	15444	Shale and limestone, similar to sample 2b, limestone accounts for 30% of sample as randomly oriented intraclasts.
4	15447	Shale and limestone, shale brownish black (5 YR 2/1), shiny accounts for 70% of sample, limestone is dark greenish gray (5 G 4/1), fossiliferous.

Acc. No.: 278. Location: C-SW-NW, Sec. 34, T11N, R16W, Washita Co. Operator: Gulf Oil Corp., #1 Fletcher, 4 in. core. Sample Depths: 12345-12349 ft., Desmoinesian.

Sample Number	Depth (ft.)	
17	12345	Shale, greenish black (5 G 2/1) and sand, greenish gray (5 G5/1), disrupted, interlaminated, sand fine to medium grain, slickensides in shale, petroliferous, 50% shale.
19	12349	Sand, medium gray (N 5) and shale, dark gray (N 3), calcareous sand with thin (1 mm.) dark micaceous shale layer, dark organic (?) subparallel flecks throughout sand, cement in shale is dolomite (x-ray), thin section 2343.

Acc. No.: 285. Location: C-SE-NE, Sec. 14, T12N, R23W, Roger Mills Co. Operator: Gulf Oil Corp., #1 Taylor, 4 in. core. Sample Depth: 12754 ft., Desmoinesian.

Sample Number	Depth (ft.)	
104	12754	S nd, dark greenish gray (5 G 5/1), and shale, greenish black (5 G 2/1), calcareous, dolomitic, very fine sand, thick (2 cm.) shale irregularly interlayered, sand contains numerous thin (< 1 mm.) black disrupted discontinuous lenses and films, shiny irregular fracture surfaces in shale, dolomite dominant carbonate in sand, calcite dominant in shale, thin section 2341.

Acc. No.: 314. Location: C-NE-NW Sec. 31, T9N, R3W, McClain Co. Operator: Petroleum, Inc., #1 Kunkel, 4 in. core. Sample Depths: 9676-9701 ft., Ordovician (Simpson).

Sample Number	Depth (ft.)	
90a	9676	Limestone, dusky yellowish green (10 GY 3/2) to olive gray (5 Y 4/1), dolomitic, fossiliferous, irregular pale yellowish green (10 GY 7/2) intraclasts, dolomite and calcite in approximately equal amounts, widely distributed quartz sand and shale.
90b	9678	Limestone, similar to sample 90a, contains 4 cm. shale layer, olive black (5 Y 2/1), irregularly laminated.
91	9680	Limestone, grayish green (10 GY 5/2), intraclastic, fossiliferous, intraclasts are light gray (N 7) and display lineation parallel to "bedding," intraclasts rimmed by narrow band, olive gray (5 Y 4/1), minor sand and clay content, thin section 2120.
93	9685	Limestone, medium gray (N 5½), coarsely grained, irregular fine-grained laminations, olive gray ((5 Y 4/1), soft-sediment deformations common, minor sand.
94a	9688	Limestone, dolomite, shale. Lower half is limestone, grayish green (5 G 5/2), coarsely crystalline; upper half is dolomite, light brownish gray (5 YR 6/1), fine-grained carbonates separated by 2 mm. shale, olive black (5 Y 2/1).
94b	9689	Limestone, similar to that of 94a.
95	9690	Limestone, grayish green (10 GY 5/2), disrupted, intraclastic.
96	9694	Mudstone, dark greenish gray (5 GY 3/1), blocky fracture.
97a	9696	Dolomite, medium dark gray (N 4), corasely crystalline, as intraclasts, contains carbonaceous flecks, shale, dark greenish gray (5 GY 3/1), shiny, irregularly engulfs dolomite.

Acc. No.: 314--Continued.

Sample Number	Depth (ft.)	
97b	9698	Shale, medium dark gray (N 4), shiny along partings, irregularly silty.
97c	9699	Dolomite, medium gray (N 5½), fractures filled with coarse spar, red-brown stains along other non-spar-filled fractures.
98a	9700	Dolomite, similar to 97c, disrupted, intraclastic.
98b	9701	Shale, dusky blue green (5 BG 3/2), well indurated, calcite and dolomite cement.

Acc. No.: 316. Location: C Sec. 17, T8N, R10E, Hughes Co.
Operator: Pan American Petroleum Corp., #4 Perryman C, 4 in. core.
Sample Depths: 3710-3860 ft., Ordovician (2nd Wilcox Sand of Simpson).

Sample Number	Depth (ft.)	
1a	3710	Sandstone, olive gray (5 Y 4/1), well indurated, irregular dark banding, well rounded sand, bimodal size, medium sand and coarse silt, dolomite and calcite cement, minor clay, thin section 2348.
1b	3712	Sandstone, similar to 1a, dark bands have finer grain size.
1c	3715	Sandstone, pale green (5 G 7/2), friable, clean, bimodal very well rounded medium sand and coarse silt, grains appear frosted, thin section 2347.
3b	3724	Sandstone, grayish yellow green (5 GY 7/2), friable, grades into well indurated (calcite cement) light brownish gray (5 YR 6/1), sand, minor clay in friable portion.
4b	3732	Sandstone, average color olive gray (5 Y 4/1), uneven banding, blotchy color, lighter areas less indurated.
5b	3736	Sandstone, light olive gray (5 Y 6/1), friable, some irregular well indurated petroliferous laminations, dark gray (n 3), calcite cement.
7	3745	Sandstone, light grayish green (10 GY 6/2), very well indurated, ferroan dolomite cement.
9	3757	Sandstone, light grayish green (10 GY 6/2), friable, grades into indurated moderate yellowish green (10 GY 6/4) sand, dolomite cement.
10	3761	Sandstone, light greenish gray (5 G 8/1), dolomitic, very well indurated, crystals line cavities, grades into well indurated moderate yellowish green (10 GY 6/4) sand, no cavities, calcite cement.
13	3786	Sandstone, light olive gray (5 Y 6/1), well indurated, white splotches surrounded by thin dark gray rims.

Acc. No.: 316--Continued.

Sample Number	Depth (ft.)	
19	3786	Sandstone, drak grayish olive green (5 GY 2/2), very well indurated, salty, irregular petroliferous areas, calcite cement.
21	3817	Sandstone, average color light olive gray (5 Y 6/1), poorly indurated to friable, petroliferous along fractures.
22	3821	Sandstone, dark grayish olive (10 Y 3/2), friable, petroliferous.
24	3842	Sandstone, similar to sample 22, some irregular white blotches capped by irregular silty laminations.
28	3858	Sandstone, medium gray (N 5), silty, argillaceous, fissile.
29	3860	Sandstone, light to medium grayish olive (10 Y 4/2), irregularly banded.

Acc. No.: 321. Location: SE-NW Sec. 19, T16N, R16W, Dewey Co., Operator: Sunray DX, #1 Richardson, 4 in. core. Sample Depths: 9719-9726 ft., Desmoinesian (Oswego).

Sample Number	Depth (ft.)	
12	9719	Shale, black (N 1), dull, uniform, petroliferous.
14a	9725	Shale, dark greenish gray (5 G 4/1), silty, irregular calcareous areas, fine oriented mica on subparallel bedding planes.
14b	9726	Shale, medium dark gray (N 4), subparallel bedding, good parting, fine oriented mica flakes common on bedding planes, petroliferous, medium light gray (N 6) silt as fine discontinuous stringers accounts for 10% of sample, thin section 2346

Acc. No.: 360. Location: SW-SW-SE Sec. 30, T14N, R4W, Oklahoma Co. Operator: Sohio Oil Co., #B-3 Cargill, 3 in. core. Sample Depths: 6752-6791 ft., Desmoinesian (Bartlesville).

Sample Number	Depth (ft.)	
1	6752	Shale, medium gray (N 5), crinoidal, disrupted bedding, some scattered silt lenses, thin section 2121.
2	6755	Shale, similar to sample 1, fossil hash abundant, calcareous silt, light gray (N 7), accounts for 30% of sample.
4	6759	Silt and shale, similar to sample 2, thick bedding ($2\frac{1}{2}$ cm.) badly contorted, shale accounts for 40% of sample.
5	6761	Silt, similar to sample 4, shale accounts for 5% of sample, less fossil debris.
6	6763	Shale, black (N 1), shiny to dull, irregular partings, no bedding visible, pyritiferous shell fragments, thin section 2122.
7	6765	Silt, similar to sample 5, shale more diffuse, no clear bedding contacts, no fossils.
8	6767	Silt, pale yellowish brown (10 YR 6/2), uniform, some irregular dark films.
9	6769	Sand, pale brown (5 YR 5/2), fine grained, subparallel diffuse banding (1 mm.), partings at bandings have oriented mica flakes.
12	6775	Sand, dark yellowish brown (10 YR 4/2), fine grained, uniform, no partings, scattered black organic (?) debris.
14	6779	Sand, similar to sample 12, black debris aligned.
16	6783	Sand, same as sample 14.
17	6787	Silt and shale, silt light gray (N 7), shale medium dark gray (N 4), sharp contact with overlying sand, some gentle crossbedding and flow structures, 50% shale, thin section 2123.

Acc. No.: 360--Continued.

Sample Number	Depth (ft.)	
18	6789	Shale and silt, similar to sample 17, 80% shale, silt in fine laminae, thin section 2124.
19	6791	Sand, same as sample 14.

Acc. No.: 500. Location: C-SE-NE Sec. 31, T16N, R11W, Blaine Co. Operator: Texaco Oil Co., #1 V. Jones, 4 inc. core. Sample Depths: 8779-8780 ft., Desmoinesian (Marmaton).

Sample Number	Depth (ft.)	
3b	8779	Sandstone, light gray (N $6\frac{1}{2}$), fine to very fine grained, and shale, dark greenish gray (5 G 5/1), disrupted, interlaminated, oblate spheroidal sand lenses within shale, slumping and differential compaction, 50% shale, thin section 2342.
3a	8780	Sand, similar to sample 3b, 5% of interval occupied by slightly distorted dark micaceous shale, dark greenish gray (5 G 5/2).

Acc. No.: 627. Location: SW-SW-NE Sec. 10, T11N, R20W, Washita Co.
Operator: Glover, Heffner, and Kennedy, McAlpine #1-10, 3 in. core.
Sample Depths: 13750-13776 ft., Desmoinesian.

Sample Number	Depth (ft.)	
3a	13750	Shale, grayish green (10 GA 1/2) and sand, medium light gray (N 6½), very fine grained, finely interlaminated, 70% shale, disrupted bedding, differential compaction, mica flakes common on surface of shale laminae.
3b	13751	Sandstone, medium light gray (N 6½), very fine grained, scattered very fine discontinuous subparallel dark clay films and laminae make up 5% of sample, bedding disrupted, mica flakes common on bedding planes, thin section 2340.
9a	13775	Shale and sand similar to sample 3a, finely interlaminated but better segregation, top 6 in. 95% shale, lower 6 in. 90% sand.
9b	13776	Sandstone, light gray (N 7), scattered diffuse dark shale laminae account for 5% of sample, partings at shale, aligned mica flakes on shale partings.

Acc. No.: 630. Location: C Sec. 14, T3S, R3W, Carter Co.
Operator: King Resources, Inc., Stewart #1-14, 4 in. core.
Sample Depths: 6542-6575 ft., Desmoinesian (Deese).

Sample Number	Depth (ft.)	
1a	6542	Shale, dark grayish green (10 G 4/2), 2 mm. layers, irregular sandy stringers, greenish gray (5 G 6/1), less than 1 mm. thick.
1b	6545	Sandstone, moderate yellowish green (10 GY 6/4), with irregular fine (0.1 mm.) shale laminae, grayish green (10 G 4/2).
2	6548	Sandstone, light brownish gray (5 YR 5/1), with irregularly interlayered shale, greenish black (5 GY 2/1), disrupted slump and flow structures, 40% shale.
4	6556	Sandstone, light brownish gray (5 YR 5/1), minor lenses and films of shale, moderate olive brown (5 Y 4/4), 10% shale.
5	6558	Sandstone, similar to sample 4, 2% shale.
6	6561	Sandstone and shale, similar to sample 5, 50% shale, subparallel organic flecks in shale.
7	6571	Shale and sandstone, similar to sample 7, 20% sand.
9	6575	Shale, grayish black (N 2), obscure bedding, shiny glassy partings at various angles.

Acc. No.: AL3. Location: 1200 ft. N, 800 Ft. W of SE corner of Sec. 14, T2N, R15W, Comanche Co. Operator: U. S. Army Corps of Engineers. Sample Depths: 172-193 ft., Permian.

Sample Number	Depth (ft.)	
45	172	Claystone, grayish green of varying hue (10 GY 5/2 to 5 G 5/2), irregular fracture, indistinct disrupted bedding.
46a	173	Claystone, similar to sample 45 but more homogeneous.
46b	175	Claystone, similar to sample 45, silty.
46c	178	Sandstone, grayish yellow green (5 GY 7/2), medium grained, angular, feldspathic, clay intraclasts, friable.
50	193	Arkose, grayish orange pink (5 YR 6/2), poorly sorted, coarse to very fine sand, clay intraclasts, friable, thin section 2345.

Acc. No.: Fargo. Location: 1200 ft. S, 2360 ft. W of intersection of U. S. 283 and Texas 91, NE $\frac{1}{4}$, Sec. 29, Blk. 29, H2TC, Reg. Co. Survey, Wilbarger Co., Texas. Operator: U. S. Army Corps of Engineers. Sample Depths: 120-207 ft., Permian.

Sample Number	Depth (ft.)	
23	120	Sandstone, very light gray green (5 G 7/3), very fine sand, common light-colored rounded clay intraclasts, sharp contact with similar but moderate red (5 R 5/4), mineralogies similar, more dolomite in light portion.
25	180	Sandstone, pale green (5 G 7/2), fine, friable, arbillaceous.
32	207	Shale, moderate red (5 R 4/6), irregular blocky fracture, small spherical "reduction spots."

APPENDIX B

THIN SECTION DESCRIPTIONS

General Statement

A total of 24 thin sections were prepared from representative lithologies and were examined in detail. Seventeen, representative of these, are described on the following pages. The thin sections were studied to determine mineral composition, texture, and if possible, the sequence of diagenetic changes. The nomenclature used is modified from Folk (1965). Color assignments were made by comparison with the G. S. A. Rock Color Chart (1963). Percentages cited are based upon a count of at least 200 points. Grain sizes were measured with a calibrated occular micrometer. All thin sections are on file by accession number at the School of Geology and Geophysics X-ray Laboratory.

Format

I. ACCESSION NUMBER AND SAMPLE IDENTIFICATION

II. ROCK NAME AND GENERAL DESCRIPTION.

III. STRUCTURES AND TEXTURE.

IV. CHEMICAL CONSTITUENTS. Authigenic and diagenetic components.

V. TERRIGENOUS CONSTITUENTS.

VI. ADDITIONAL COMMENTS.

I. 2121, core 360, sample 1, depth 6,752 ft.

II. Poorly washed biosparite; quartzose, disrupted "bedding."

III. Disorganized mixture of calcite-replaced fossils, irregular concentrations of medium-sized silt, contorted bands of iron-oxide-stained illitic clay.

IV. Calcite, 75%; approximately one-half micritic and one-half recrystallized larger grains (to 0.1 mm), coarser grains completely filling fractures and cavities and as fossil debris replacement.

Siderite, 1%; isolated scattered grains replacing calcite.

Pyrite, 1%; widely scattered euhedral grains and aggregates, more abundant in shaley portion.

V. Quartz, 13%; angular to subangular, medium silt, embayed by calcite, commonly confined in irregular concentrations.

Illite, 5%; finely divided, ferric-oxide stain common, concentrated in contorted laminations.

Chlorite, 2%; elongate mica laths, more numerous in shaley portions, parallel to laminations.

Muscovite, 2%; laths scattered through silt and clay, more abundant in shale, parallel to laminations.

Volcanic Rock Fragments, trace; fine-grained granular assemblages, rounded, coarse silt size.

Collophane, trace; silt-size, rounded grains, confined to calcitic areas.

I. 2122, core 360, sample 6, depth 6,763 ft.

II. Shale; shiny to dull black, pyritiferous shell and woody fragments, irregular megascopic partings.

III. Dark red-brown stain (organic?) makes identification difficult. Elongate grains of mica and organic debris randomly oriented.

IV. Kaolinite, 4%; fine crystalline aggregates, indistinct boundaries.

Calcite, 4%; irregular areas of optically continuous cement almost obscured by clay and silt.

Pyrite, 3%; clusters of euhedral crystals replacing floral and faunal debris.

Siderite, 2%; small clusters of fine granules superimposed upon all mineral types except pyrite.

V. Clay Matrix, 49%; evenly distributed, illite, chlorite, mixed-layer illite-montmorillonite from x-ray.

Quartz, 15%; very fine to fine silt, scattered grains to 0.1 mm, commonly display strong undulatory extinction, subangular to angular.

Organic opaques, 9%; widely and randomly distributed elongate indistinct areas, petroliferous.

Metamorphic Rock Fragments, 5%; silt size, phyllitic and composite quartz grains.

Collophane, 4%; rounded, clear, wide size range, very fine sand through very fine silt.

Muscovite, 3%; fresh, undisturbed, randomly oriented laths.

Chlorite, 2%; undistorted, fresh, randomly oriented laths, average size of all mica 0.07 mm x 0.01 mm.

I. 2123, core 360, sample 17, depth 6,787 ft.

II. Subgraywacke; fine to very fine sand, medium dark gray with carbonaceous flecks and in places clay films.

III. Silt displays no particular orientation, continuous clay film is slightly undulose indicating only minor distortion by compaction.

IV. Calcite, 6%; sparry optically continuous cement engulfing and replacing quartz and feldspars.

Kaolinite, 5%; crystalline aggregates adjacent to and in places replacing quartz grains. Also replacing clay matrix and rarely orthoclase.

Pyrite, 2%; randomly scattered, most commonly associated with iron-oxide-stained clay matrix. Excellent octahedral crystals to 0.02 mm.

Siderite, 2%; small anhedral granules, commonly in large aggregates, commonly associated with pyrite, replaces all minerals but pyrite.

V. Quartz, 57%; overgrowths common, formed before appreciable compaction since clay and mica are bent around overgrowths, common crenulated contacts between adjacent quartz grains, extinction sharp to composite, bubble trains and crystalline inclusions common, grains attacked by calcite, siderite, kaolinite.

Clay matrix, 8%; illitic, some recrystallization, bent around detrital grains, commonly iron-oxide stained.

Orthoclase, 6%; commonly sericitized.

Chlorite, 5%; as mica laths, bent and broken by compaction, pyrite inclusions common.

Metamorphic Rock Fragments, 4%; chloritic phyllite fragments, some composite quartz aggregates.

Plagioclase, 3%; elongate grains, altered, pyrite common along twin boundaries.

Muscovite, 1%; laths bent around quartz and feldspar.

Also trace amounts of pyroxene (?), leucoxene, magnetite-ilmenite, collophane, apatite, zircon, limestone fragments, volcanic rock fragments, rutile.

2123 -- Continued.

VI. Diagenetic sequence evident in part; quartz overgrowths developed early before compaction; pyrite formed after compaction, localized commonly by compaction-caused breaks in chlorite mica; calcite replaces quartz, sericitized feldspars and illite; relationship between calcite and kaolinite uncertain, kaolinite aggregates not affected by compaction thus post-compaction formation, always associated with quartz and commonly sericitized orthoclase.

I. 2124, core 360, sample 18, depth 6,789 ft.

II. Interlayered mudstone and graywacke; dark mudstone with discontinuous coarse silt laminations.

III. Mudstone portion shows excellent alignment of clays via common extinction position, accentuated by elongate carbonaceous areas, clay and mica bent around silt grains in graywacke portion.

IV. Silt

Siderite, 4%; composite granules.

Pyrite, 2%; randomly distributed and in elongate veins associated with organic debris.

Chlorite, 2%; coarse flaring areas of fibrous grains growing from fine-grained detrital areas.

Calcite, 2%; scattered areas of cement, attacking quartz.

Kaolinite, 1%; granular aggregates.

Mudstone

Calcite, 3%; small scattered areas of cement.

Pyrite, 1%; individual scattered euhedral crystals.

V. Silt

Quartz, 44%; angular to subangular grains, minor inclusions, commonly strained, attacked where adjacent to calcite.

Metamorphic Rock Fragments, 18%; chloritic-phyllite and chlorite-composite-quartz aggregates.

Clay Matrix, 18%; illitic, areas of probable recrystallization.

Muscovite, 3%; deformed laths.

Chlorite, 3%; deformed laths.

Orthoclase, 2%; commonly altered to clay.

Limestone Fragments, 1%; rounded grains.

Plus trace amounts of tourmaline, zircon, rutile, leucoxene, magmetite-ilmenite.

V. Mudstone

Illitic Clay, 69%; excellent orientation shown by common extinction.

Quartz, 8%; angular clay-size fragments.

Carbonaceous Opaques, 8%; elongate areas parallel to bedding.

Muscovite, 7%; aligned, undisturbed laths.

Chlorite, 2%; aligned, undisturbed laths.

Phyllite Fragments, 1%; chloritic, rounded, elongate.

Collophane, 1%; widely scattered, clear, rounded grains.

VI. Authigenic components comprise at least 11% of silty portion but only 4% of clay-rich portion clearly reflecting better permeability in coarser material. Fine grain size and iron-oxide stain obscure diagenetic sequence. Calcite replaces quartz and orthoclase in silt, and siderite replaces calcite. Kaolinite always adjacent to one or more quartz grains suggesting direct source of silica. Some replacement of quartz by kaolinite is present in silt.

I. 2127, core 142, sample 1, depth 1,537 ft.

II. Feldspathic Subgraywacke; megascopically uniform, light gray with irregular light olive gray very-fine-grained laminae.

III. Medium to fine sand, some medium silt, finer grained laminae mostly micritic siderite, sand-micrite contact sharp, no distinct laminations within sand or micrite.

IV. Siderite, 7%; very fine grained aggregates surrounding and attacking most detrital grains, some phyllite fragments almost entirely consumed.

Kaolinite, 3%; granular aggregates between clastic grains, commonly replacing quartz or phyllite fragments.

Calcite, 1%; widely scattered isolated patches of cement.

V. Quartz, 51%; angular, medium to fine sand, commonly attacked by siderite, sharp extinction common, vacuoles rare, variable crystalline inclusions, overgrowths common.

Metamorphic Rock Fragments, 20%; mostly elongate chloritic phyllite grains, some composite quartz, phyllite attacked by carbonates and kaolinite.

Orthoclase, 8%; fine sand to medium silt, grains altered to clay, attacked by siderite.

Volcanic Rock Fragments, 5%; fine polycrystalline fragments.

Clay Matrix, 2%; illitic, good orientation shown by common extinction, mostly replaced by siderite.

Plutonic Rock Fragments, 1%; coarse quartz-feldspar aggregates and graphic intergrowths.

Plagioclase, 1%; only minor alteration, some attack by siderite.

Also trace amounts of altered perthite and microcline, distorted randomly oriented muscovite.

VI. Percentages cited above are for sand portion. Carbonate laminae are more than 70% siderite with very fine silt clastics widely scattered. Siderite obscures much detail in sand, however diagenetic sequence is quartz overgrowths first, kaolinite next, and siderite last.

I. 2128, core 142, sample 6, depth 1,594 ft.

II. Feldspathic Subgraywacke; megascopically uniform light olive gray sand.

III. No lineations visible, fine sand grains angular to subrounded in places, average grain size 0.17 mm.

IV. Kaolinite, 5%; granular aggregates, attacking quartz, phyllite fragments, plagioclase, orthoclase and especially clay matrix.

Siderite, 3%; anhedral granular clusters, commonly along grain boundaries.

Calcite, trace; diffuse, throughout clay matrix.

Pyrite, trace; euhedral crystals, commonly associated with leucoxene.

Chlorite and Illite, trace; fibrous clusters replacing clay matrix.

V. Quartz, 44%; subangular to subrounded, overgrowths common, some crenulated "pressure solution" contacts, attacked by siderite and kaolinite, minor inclusions, extinction commonly sharp.

Metamorphic Rock Fragments, 19%; one-fourth are composite quartz, remainder phyllite fragments, scattered phyllite replaced by kaolinite, chlorite or illite.

Volcanic Rock Fragments, 2%; fine-grained polycrystalline aggregates of quartz and feldspar.

Orthoclase, 8%; commonly altered.

Clay Matrix, 8%; illite and chlorite with scattered carbonate, some areas of recrystallization.

Chert, 2%; rounded grains, attacked by kaolinite.

Plagioclase, 1%; less alteration than in orthoclase.

Also traces of plutonic rock fragments, magnetite-ilmenite, leucoxene, chlorite, muscovite, and biotite micas.

VI. All clay types appear well crystalline on x-ray diffractograms. This is supported optically by frequent areas of recrystallization and authigenic keolinite. The apparent order of diagenetic change is quartz overgrowths first and siderite last. Recrystallization of clays, formation of kaolinite, introduction of calcite, and growth of pyrite are intermediate in undetermined order. Anomalously fresh plagioclase relative to potassium feldspars is common.

I. 2131, core 142, sample 15c, depth 1,624 ft.

II. Argillaceous Pelmatazoan Calcarenite; numerous fossil fragments in fine petroliferous groundmass.

III. Completely disrupted bedding although excellent alignment within contorted laminations is shown by organic debris, micas, and clays.

IV. Calcite, 60%; most as shell fragment replacement, remainder as micritic and coarsely recrystallized sparry cement.

Pyrite, 10%; replacing fossil debris partly or completely.

V. Clay Matrix, 19%; stained by petroliferous organic residue, x-ray shows degraded illite and chlorite, concentrated in laminae.

Quartz, 6%; fine to very fine silt, unevenly distributed.

Organic Opaques, 5%; elongate areas, commonly within shaley portions, petroliferous odor.

Muscovite and Chlorite, trace; fine laths within quartz silt areas.

VI. Diagenetic changes limited to calcite recrystallization and pyrite formation. Petroliferous stain makes detailed description difficult. Fossil debris in order of decreasing abundance includes fragments from pelmatazoans, gastropods, pelecypods, bryzoans, brachiopods, crinoids, and trilobites. Permeability has probably remained low since clays remain in degraded condition.

I. 2133, core 142, sample 18a, depth 1,640 ft.

II. Subarkose; medium to fine sand, light olive gray to light brownish gray, brownish areas due to high concentration of siderite, texture magascopically uniform.

III. Subangular to subrounded medium and fine sand with some intergranular fine and medium silt, grains cemented by large optically continuous areas of calcite, abundant siderite, and some clay.

IV. Siderite, 9%: scattered throughout but highly concentrated in a 0.5 cm. zone parallel to bedding, granular clusters along grain boundaries and fractures, rarely within plagioclase grains, replacing calcite, feldspars, quartz, kaolinite, and rock fragments.

Calcite, 7%: sparry cement, optically continuous areas engulfing numerous sand grains, attacks all types of clastic grains--especially feldspars.

Kaolinite, 5%: polycrystalline aggregates between sand grains, replacing quartz and feldspars.

Pyrite, trace: randomly scattered individual and polycrystalline grains.

V. Quartz, 51%: subangular to subrounded, angularity magnified by overgrowths and calcite attack, some replacement by siderite and kaolinite, grains commonly strained, vacuoles common, scattered zircon and rutile inclusions.

Metamorphic Rock Fragments, 8%: chlorite schists and quartz aggregates with crenulated contacts.

Orthoclase, 6%: altered to clay to varying extents, edges corroded by calcite and kaolinite.

Volcanic Rock Fragments, 4%: very fine crystalline aggregates.

Plutonic Rock Fragments, 3%: coarsely crystalline quartz-feldspar aggregates and intergrowths.

Microcline, 2%: commonly severely altered.

Perthite, 2%: commonly severely altered.

Clay (Illite?), 2%: fine widely disseminated matrix.

Also traces of zircon, rutile, chert.

2133--(Continued).

VI. In addition to authigenic kaolinite, some recrystallization of chlorite within schist fragments and of "muscovite" within clay is present, order of authigenic growth chronologically is quartz overgrowths, kaolinite formation, calcite cement, siderite. No clear evidence for relative position of pyrite or recrystallized chlorite and illite is present.

I. 2340, core 627, sample 3b, depth 13,751 ft.

II. Argillaceous Subarkose: very fine grained, disrupted irregular subparallel clay laminations, iron-oxide stain irregularly distributed.

III. Disrupted irregular bedding defined by argillaceous concentrations suggests slumping of unconsolidated material. Detrital muscovite and chlorite parallel to bedding, and fine grain size suggest low energy depositional environment. Average grain size 0.08 mm.

IV. Siderite, 2%: widely scattered aggregates of fine silt-size anhedral grains replacing calcite.

Calcite, 2%: sparry to cloudy cement, replacing quartz.

Kaolinite, 1%: fine-grained clusters, commonly adjacent to altered feldspars.

V. Quartz, 61%: subrounded to subangular, grains commonly interlock with scattered feldspars included suggesting plutonic rock fragments, commonly etched by calcite, variable extinction.

Clay Matrix, 14%: illite(?), scattered throughout sand and concentrated in thin discontinuous layers, commonly iron-oxide stained.

Orthoclase, 8%: subrounded grains, commonly altered to clay.

Chlorite, 4%: as individual mica laths.

Metamorphic Rock Fragments, 1%: chloritic phyllite and composite quartz.

Volcanic Rock Fragments, 1%: composite quartz-feldspar, fine-grained aggregates.

Muscovite, 1%: laths, commonly bent.

Plagioclase, 1%: altered subangular grains, some closely associated with quartz.

Leucoxene, 1%: widely scattered subrounded grains.

Magnetite-ilmenite, 1%: widely scattered subrounded grains.

Limestone Rock Fragments, 1%: widely scattered, subrounded to rounded, micritic.

Organic Opaques, trace: carbonaceous plant fragments.

2340--(Continued).

VI. Varied source area--igneous, metamorphic, sedimentary. No clear evidence of quartz overgrowths, calcite replaces quartz and feldspar, siderite replaces calcite, chronologic relationship between carbonates and authigenic kaolinite not clear. Other alterations are argillization of feldspars and formation of leucoxene.

I. 2341, core 285, sample 104, depth 12,754 ft.

II. Argillaceous Subarkose: medium light gray coarse silt with subparallel dark shaly lenses and laminae (less than 1.0 mm) showing small-scale crossbedding and disruptions.

III. Majority of thin section occupied by a close mixture of fine clay (illite from x-ray) and carbonate. An accurate point count is difficult due to strong masking by carbonate replacement. Dark laminae consist of iron-oxide stained aligned clay with abundant polycrystalline pyrite masses and some carbonaceous material.

IV. Calcite and Dolomite, 24%: anhedral "groundmass" with some sparry crystals and dolomite rhombs, replacing all detrital material. Rhombs are 0.04 mm and smaller.

Pyrite, 14%: as polycrystalline masses, commonly 0.10 mm, widely distributed but more common in argillaceous carbonaceous laminae. apparently replacing organic debris.

V. Illite, 30%: abundant throughout slide but concentrated in thin iron-oxide-stained laminae. Obscured by carbonates, good alignment.

Quartz, 15%: angular to subrounded grains, strongly etched by carbonates, 0.04 mm common size, percentage is minimal.

Plagioclase, 6%: angular coarse silt grains, most grains fresh except for peripheral carbonate attack.

Orthoclase, 5%: grains angular to subrounded, attacked by carbonate, altering to clay.

Perthite, 2%: angular to subrounded, attacked by carbonate, altering to clay.

Organic Opaques, 1%: carbonaceous, elongate, commonly surrounded or being replaced by pyrite, more common in shaly laminae.

Micas, 1%: muscovite with some chlorite and biotite, subparallel alignment, minor distortion, attacked by carbonates.

Leucoxene, 1%: subrounded, widely distributed, coarse silt.

Also traces of maghematite, magnetite-ilmenite, apatite, graphic quartz-feldspar plutonic grains, metamorphic rock fragments, limestone fragments.

I. 2342, core 500, sample 3b, depth 8,779 ft.

II. Feldspathic subgraywacke: fine to very fine light colored (N 6.5) sand interlaminated with iron-oxide-stained, organic-rich, micaceous shale layers.

III. Subparallel laminations with oblate fine sand lenses within shale laminations, sand grains angular to subrounded, mica and clay shows excellent alignment, sand-shale contacts sharp except in vicinity of sand "intraclasts."

IV. Carbonate, 4%: as calcite cement and some widely scattered siderite granules.

Kaolinite, 3%: clusters of fine (less than 0.002 mm) granules, commonly bordering and intruding into argillized feldspars and phyllite fragments.

Pyrite, trace: very fine aggregates, rarely in shale.

V. Quartz, 44%: fine sand, coarse silt in shaly laminae, angular to subrounded, etched by calcite, grains commonly severely strained.

Clay Matrix, 13%: chlorite and illite, secondary crystallization suggested at places by coarse fibrous appearance, bent around sand grains, excellent alignment within shale laminae.

Metamorphic Rock Fragments, 12%: composite quartz grains, chloritic phyllite and schist grains.

Orthoclase, 7%: subangular to subrounded grains, mostly in sand portion, grains attacked by authigenic kaolinite and in places by illitic and chloritic recrystallization.

Mica, 5%: approximately equal amounts of chlorite, biotite and muscovite as distorted laths in sand portion, gently warped in shale portion.

Volcanic Rock Fragments, 3%: fine-grained aggregates of quartz and feldspar.

Plagioclase, 2%: scattered angular laths, selectively argillized along twin boundaries.

Organic Opaques, 2%: elongate carbonaceous particles, almost exclusively within shale.

2342--(Continued)

V. (Continued).

Magnetite-ilmenite, 2G: coarse silt, subrounded, scattered throughout sand and shale.

Hematite, 1%: fine sand, subrounded in sand portion, as stain in shale.

Limestone Fragments, 1%: rounded fine sand grains, micritic.

Also trace amounts of leucoxene, collophane, staurolite, epidote, and zircon.

VI. Varied source area, metamorphic fragments predominate, some suggestions of recrystallization and grain growth among chlorite and illite, kaolinite new mineral growth most commonly associated with chlorite rock fragments or potassium feldspar. Concentration of organic debris and little, if any diagenesis in shale suggests intrastratal fluid movement confined to sands with little sand-shale interchange.

I. 2343, core 278, sample 19, depth 12,349 ft.

II. Calcareous Arkose: medium gray, medium sand, thin laminations and films of dark gray micaceous shale, megascopic black carbonaceous flakes throughout sand.

III. Randomly oriented, poorly sorted, subangular grains, size range from 0.01 mm to 0.60 mm (average 0.30 mm) in addition to clay, organic flakes display subparallel alignment megascopically but no alignment is noted in micrscopic investigation.

IV. Calcite, 43%: cement throughout sample, attacking quartz and feldspars, x-ray shows minor dolomite.

Pyrite, 1%: commonly associated with organic material.

Kaolinite, trace: polycrystalline patches, commonly associated with orthoclase.

V. Quartz, 16%: subangular grains, vacuoles common, few grains have abundant crystalline inclusions, attacked by calcite.

Perthite, 8%: varying amounts of alteration, scattered grains show highly altered sodic portion, nearly fresh potash.

Orthoclase, 8%: wide size range, from largest to smallest in slide (0.6 mm--0.01 mm), commonly intensively altered to clay.

Graphic Intergrowths, 8%: variety of geometric patterns of quartz in orthoclase and microcline, scattered square euhedral beta quartz in orthoclase, feldspar portion commonly sericitized.

Chert, 4%: subrounded to rounded grains, some carbonate attack.

Limestone Fragments, 4%: rounded micritic grains.

Volcanic Rock Fragments, 4%: fine-grained aggregates, tridymite(?) needles common.

Clay, 2%: illite as unevenly distributed matrix.

Plagioclase, 1%: altered but commonly less intense than orthoclase.

Microcline, 1%: commonly intensely altered, attacked by carbonate.

Also traces of magnetite-ilmenite, leucoxene, zircon, muscovite, biotite, chlorite micas.

2343--(Continued)

VI. Calcite overwhelms nearly everything, plagioclase not as strongly altered as K-feldspar. From x-ray investigation, shale associated with this sand contains dolomite and minor calcite as opposed to calcite and minor dolomite in sands. Local derivation of Mg from clays of shale probable. Graphic intergrowths similar to Wichita Mountain granites, especially Lugert Granite.

I. 2344, core 142, sample 19c, depth 1,537 ft.

II. Siderite Concretion: micritic siderite with irregularly scattered very fine sand and pyrite.

III. Randomly oriented mica laths and randomly-shaped areas of clastic concentration suggest post-depositional distortion. Large (to 0.38 mm) elongate carbonaceous areas randomly distributed, commonly replaced by fine polycrystalline pyrite.

IV. Siderite, 91%: micritic, attacking detrital quartz and feldspar, void fillings are coarser grains (0.004 mm). Percentage a maximum, some detrital material probably obscured.

Pyrite, 3%: as euhedral crystals (0.008 mm) and fine-grained polycrystalline aggregates, the latter confined to carbonaceous areas.

Kaolinite, 2%: irregular polycrystalline patches, 0.2 mm and smaller.

V. Quartz, 2%: subangular to subrounded, irregular outlines due to siderite attack, sharp extinction common, minor rutile inclusions, grains widely scattered but commonly concentrated in poorly-defined areas.

Collophane, 1%: randomly distributed, rounded, somewhat larger than quartz grains.

Also traces of muscovite, biotite, metamorphic rock fragments, volcanic rock fragments, orthoclase, chert, carbonaceous material. (The latter was probably initially present in higher percentage but now replaced by pyrite).

VI. Micritic size of siderite suggests "primary" formation. Siderite attacking essentially all detrital grains. Pyrite replacing organic material suggests reducing environment near organic debris with sulfur from organics and iron from siderite. Authigenic kaolinite clusters have shapes suggesting void fillings, some clusters appear to be replacing feldspars.

I. 2345, core AL3, sample 50, depth 100 ft.

II. Graphic Arkose: medium to coarse sand, megascopically homogeneous.

III. Plutonic graphic intergrowth fragments dominate as angular to subangular grains 0.9 mm to 0.2 mm, averaging 0.4 mm. Widely distributed individual quartz scattered as subrounded to rounded grains 0.1 to 0.2 mm diameter. Clay present commonly as coating on grains, commonly iron-oxide stained.

IV. Kaolinite and "Illite," 8%: as coating around grains and in cleavage planes, attacking feldspars, well crystalline elongate plates and vermicular tablets.

Calcite, 2%: as sporadic cement, attacks feldspar.

Pyrite, trace: replacing magnetite(?).

V. Plutonic Graphic Rock Fragments, 36%: majority are graphic intergrowths of quartz and perthite or quartz and orthoclase, feldspars argillized to varying extent.

Quartz, 18%: majority as composite grains, some rounded grains apparently recycled sedimentary grains.

Perthite, 10%: sodic feldspar commonly more altered.

Volcanic Rock Fragments, 10%: fine-grained polycrystalline fragments.

Orthoclase, 9%: commonly argillized and rimmed by authigenic clay.

Microcline, 6%: commonly argillized and rimmed by authigenic clay.

Also traces of biotite, muscovite, magnetite-ilmenite, leucoxene, rutile, zircon, tourmaline.

VI. Micas bent around other grains. Coarsely crystalline clay around grains and along fractures commonly iron-oxide stained and slightly pleochroic thus not optically a typical kaolinite. X-ray patterns show very-well crystalline kaolinite accounting for nearly all the clay mineral content, slight pleochroism suggests dickite.

I. 2346, core 321, sample 14b, depth 9.726.

II. Pyritiferous Feldspathic Subgraywacke: subparallel interlaminated dark greenish gray coarse silt and very fine sand and greenish black shale, disrupted laminations.

III. Subparallel, in places disrupted laminations defined by concentration of clay, laminations distinct megascopically but gradational in thin section, alignment of platy and elongate minerals in shaly portion is good, moderate in coarser portion.

IV. Calcite, 16%: cement, almost totally confined to sand-silt portion.

Pyrite, 8%: polycrystalline aggregates in silt and edges of shale, commonly associated with organic debris.

Chlorite, 1%: fibrous masses, commonly within detrital fine-grained clay and fractures of feldspars.

Siderite, 1%: individual anhedral grains (0.005 mm) replacing calcite.

Kaolinite, trace: polycrystalline aggregates, in silt, commonly adjacent to orthoclase and perthite.

V. Quartz, 40%: angular to subrounded coarse silt and very fine sand, vacuoles common, undulose to sharp extinction, replacement by calcite common.

Orthoclase, 8%: altered to varying extent, attacked by calcite.

Metamorphic Rock Fragments, 7%: subrounded composite quartz and phyllite fragments.

Muscovite, 4%: laths in silty areas, undisturbed to bent to broken depending upon proximity to silt grains.

Clay Matrix, 4%: illite (x-ray), good alignment in shaly laminations only.

Chlorite, 2%: laths similar to muscovite.

Biotite, 2%: laths similar to muscovite.

Plagioclase, 2%: less altered than orthoclase.

Perthite, 1%: selectively attacked.

Volcanic Rock Fragments, 1%: polycrystalline fine-grained aggregates.

2346--(Continued).

V. (Continued).

Limestone Fragments, 1%: well-rounded coarse silt and very fine sand, micritic.

Also traces of plutonic rock fragments (orthoclase-quartz aggregates and some graphic intergrowths), chert, leucoxene, organic carbonaceous debris, tourmaline, magnetite-ilmenite.

VI. Calcite attacking quartz and feldspar and replacing matrix clay. Authigenic and recrystallized clay not attacked by calcite, thus probably postdates calcite. Siderite confined to calcite. Organic material pyritized in silt portion but only rarely in argillaceous areas. K-feldspars more altered than plagioclase.

I. 2347, core 316, sample 1c, depth 3,715 ft.

II. Orthoquartzite: friable, magascopically uniform olive gray sand.

III. Very-well-rounded medium quartz sand (average 0.4 mm) with interstitial subrounded to subangular coarse quartz silt (average 0.05 mm) very weakly "cemented" with clay matrix.

IV. No authigenic components optically identified.

V. Quartz Sand, 71%: very well rounded, high sphericity, some interpenetration of grains, wavy extinction, most grains clear, some with abundant vacuoles, oriented rutile needles, scattered tourmaline and zircon inclusions,no overgrowths.

Quartz Silt, 19%: subrounded to subangular, minor inclusions.

Clay Matrix, 10%: illite (by x-ray).

Chert, trace: silt size.

VI. Quartz probably originally of plutonic origin. Small amount of orthoclase and dolomite are indicated by x-ray investigation, not identified optically. Lack of cement and authigenic components suggest little fluid movement through sands, despite friability porosity and permeability are low due to interstitial clay. Compare with thin section 2348.

I. 2348, core 316, sample 1a, depth 3,710 ft.

II. Orthoquartzite: megascopically uniform olive gray sand with scattered irregular dark laminations, well indurated.

III. Very-well-rounded medium quartz sand (average 0.4 mm) with interstitital subrounded to subangular coarse quartz silt (average 0.05 mm), tightly cemented with calcite and dolomite and quartz overgrowths.

IV. Dolomite, 10%: abundant rhombs, replacing calcite, attacking quartz.

Quartz overgrowths, 8%: on all grain sizes, commonly interlocks grains.

Calcite, 4%: as optically continuous areas, attacking quartz, being replaced by dolomite.

V. Quartz Sand, 60%: very well rounded grains, common overgrowths, undulose to composite extinction, some vacuoles, abundant zircon, some rutile needles and grains.

Quartz Silt, 16%: angular to subrounded, abuncant overgrowths.

Clay (illite), 2%: interstitial matrix, being attacked by carbonates.

VI. Compare with thin section 2347. The clay in this interval of the core is largely segregated into shale laminae (none in this thin section) allowing much higher permeability and porosity. Quartz overgrowths occur first, "pressure solution" second, calcite third, dolomite most recently.

APPENDIX C

ANALYTIC PROCEDURES

General Statement

Samples for study were selected from cores on file at the University of Oklahoma Core and Sample Library. A total of 14 cores from varying depths and geographically dispersed locations (see Fig. 2) were chosen for detailed investigation. From these cores, more than 125 samples were thoroughly examined by various x-ray diffraction techniques. Twenty-eight of the samples were subjected to x-ray fluorescence analysis. The location of the cores and descriptions of the samples are given in Appendix A.

X-Ray Diffraction

Representative samples from each lithologic unit were separated and ground in an agate mortar until all material passed an 80-mesh dry sieve. A split fraction of each was sieved onto a glass slide coated with a film of petroleum jelly which serves as an inert adhesive. X-ray analyses were made of these randomly-oriented bulk powder samples to determine overall mineral composition and to locate "edge" reflections of the clay minerals.

A second split fraction of each was dispersed in distilled water by an ultrasonic transducer (Branson Sonifier, model S125). The samples were variously size-fractioned (spherical equivalent) by settling techniques based upon Stokes' Law (Folk, 1965, p. 40). Flocculation was encountered in a few samples and was eliminated by repeated washings with distilled water. Suspensions of these size fractions were allowed to settle and dry at 60° C on glass slides in order to enhance basal reflections of the clay minerals. Duplicate oriented slides were prepared of the less-than-4-micron fraction for each sample. One slide was x-rayed before and after heating to temperatures varying from 100° C to 700° C. The other slide was x-rayed after a minimum of 3 hours exposure to a saturated ethylene glycol atmosphere at 60° C.

A third split sample of approximately one-fourth of the samples was treated with warm 10% HCl for 12 hours and then sedimented on glass slides. This procedure was used to confirm the presence of kaolinite by removing the interference of chlorite.

Both North American Phillips (Norelco) and Siemens-Halske diffraction units were employed in these investigations. Nickel-filtered Cu (K-alpha) radiation generated at 40 KV and 20 ma on the former and 35 KV and 18 ma on the latter was used. The diffracted radiation was detected with scintillation counters. A scanning rate of 1° 2θ/min was used with scale factor and multiplier values varied to obtain optimum resolution on the diffractogram strip charts. Diffractograms were obtained from 2° to 65° 2θ for powder samples and from 3° to 30° 2θ for oriented samples.

Examples of diffractograms of a typical sand-shale pair are shown on the following four pages.

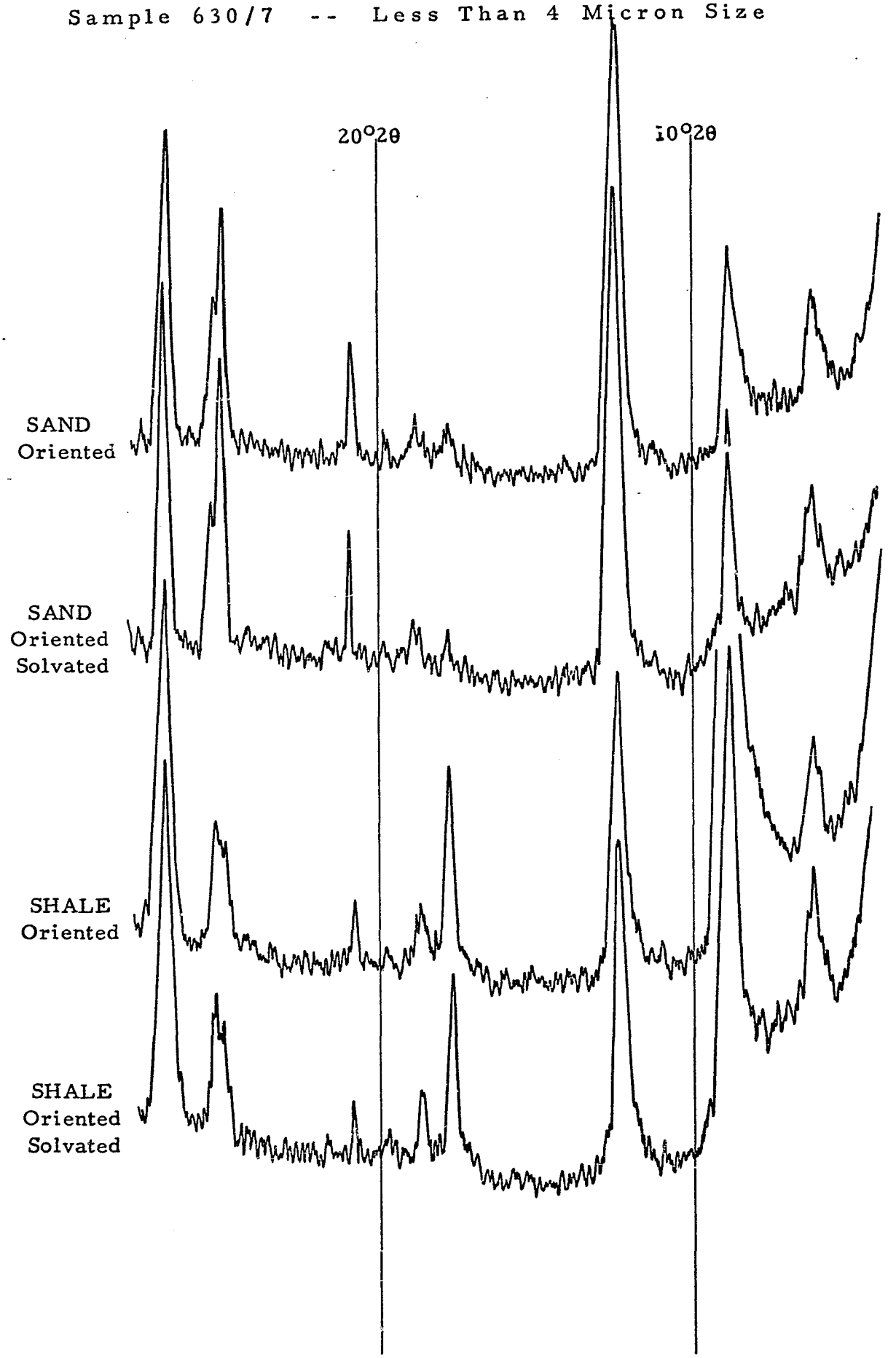
X-Ray Fluorescence

A total of 28 samples were selected for bulk chemical analysis by x-ray fluorescence. Of these, 5 are from Permian strata, 3 from Ordovician strata, and the remaining 20 represent 10 sand-shale pairs from Desmoinesian strata. The analyses of 9 samples have been rejected because of questionable total percentages. Most of these rejected analyses indicated unusually high amounts of carbonate and/or sulfur. The totals for these samples are well over 100% due to an appreciable difference in matrix effect between the samples and the standards used causing less fluorescence radiation to be absorbed in the samples than in the standards.

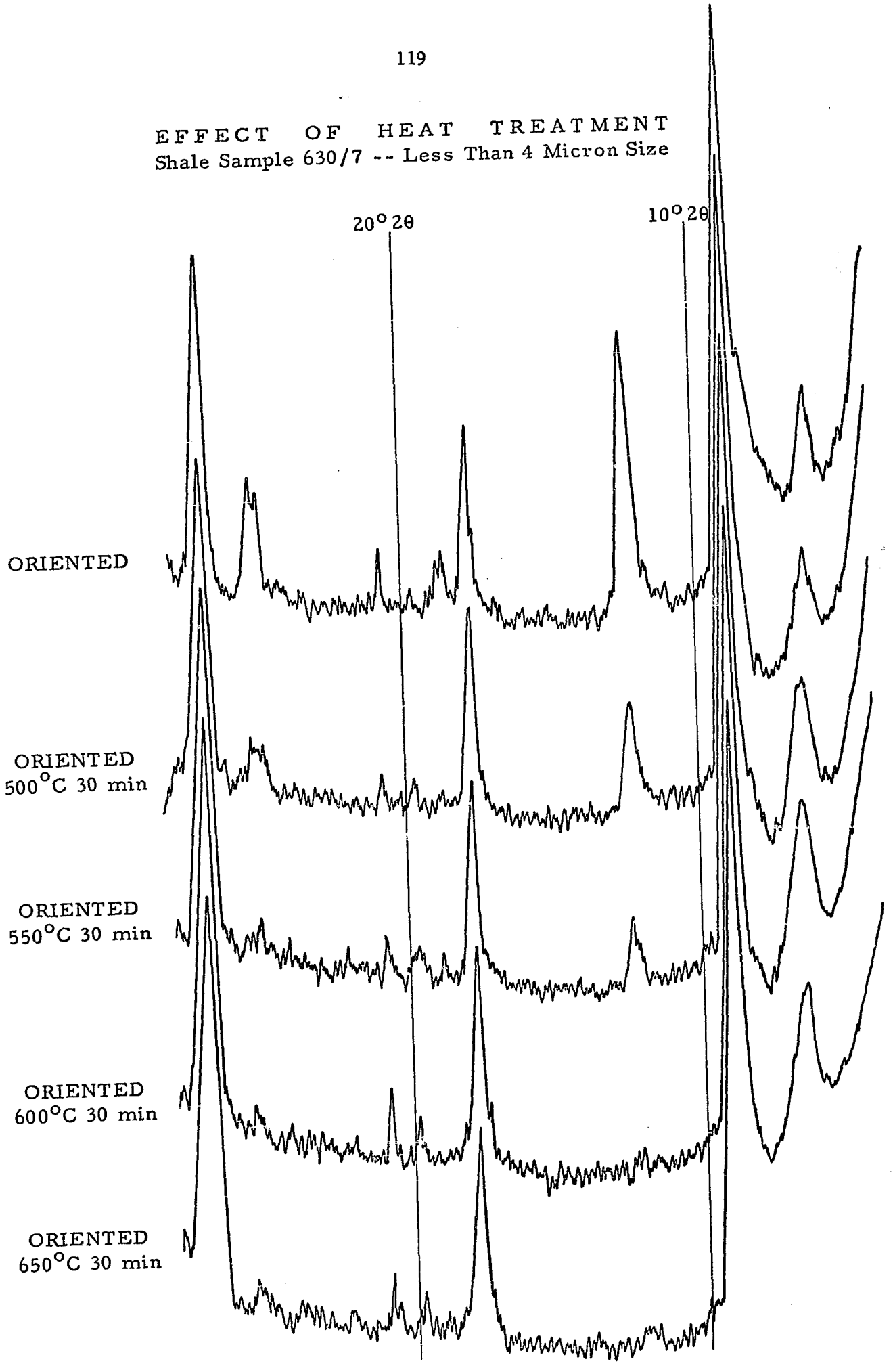
Samples were prepared by grinding in an agate mortar until all material passed a 200-mesh sieve. Each sample was then combined with sufficient binder (polyvinyl alcohol) to achieve a mixture containing 80% sample. These mixtures were then pressed into discs at approximately 15 tons/in.^{2} pressure. Standard samples had previously been prepared in a similar manner. These samples were obtained from the U. S. Geological Survey silicate rock standards and the U. S. Bureau of Standards.

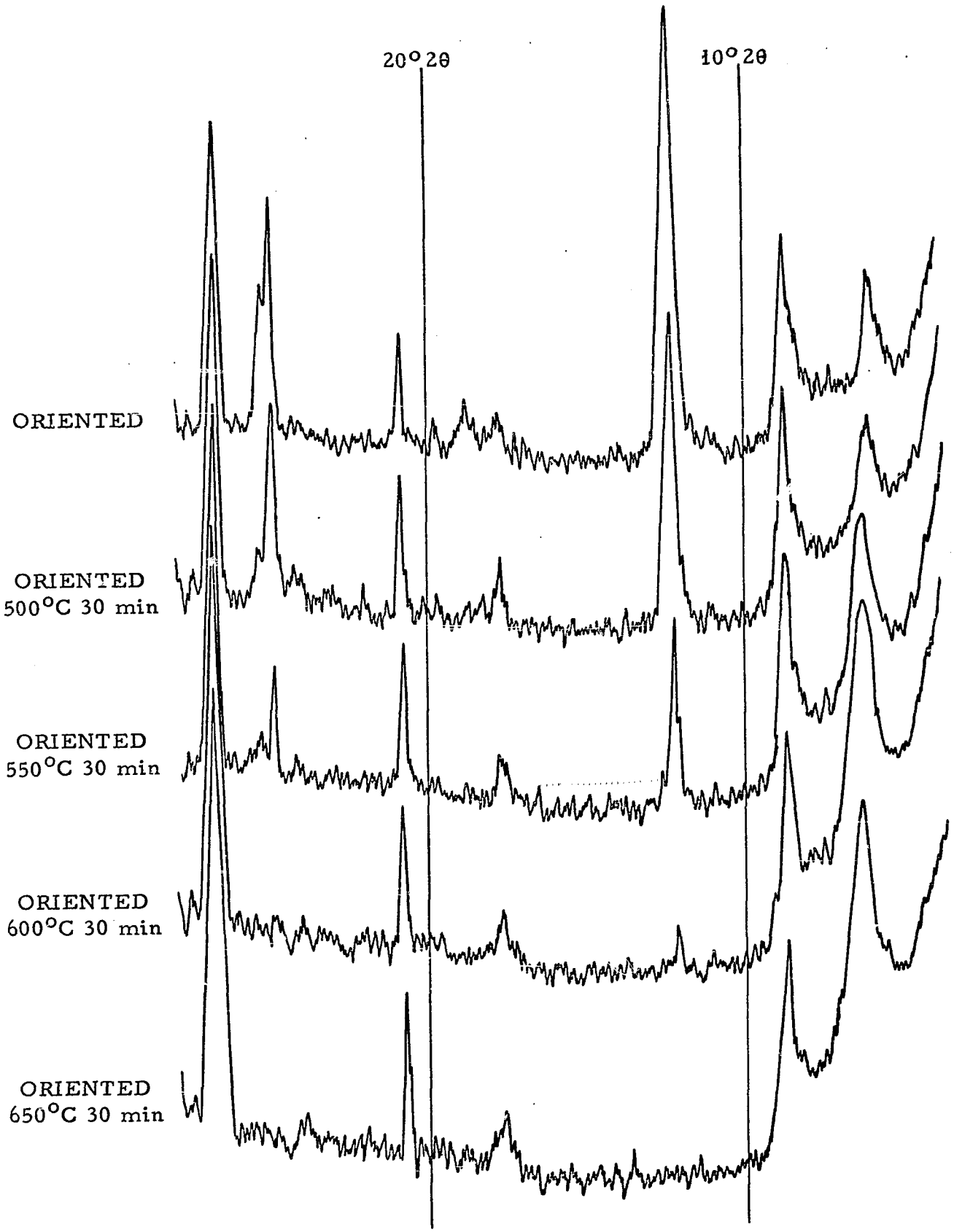
Analyses were run on a Siemens-Halske sequential x-ray fluorescence spectrometer, model SRS-1. For calcium and lighter elements, a vacuum of less-than-100 microns was kept on the system. A chromium tube and gas-flow detector were used for all elements except manganese and iron for which a tungsten tube and scintillation counter were

EFFECT OF ETHYLENE GLYCOL SOLVATION
Sample 630/7 -- Less Than 4 Micron Size



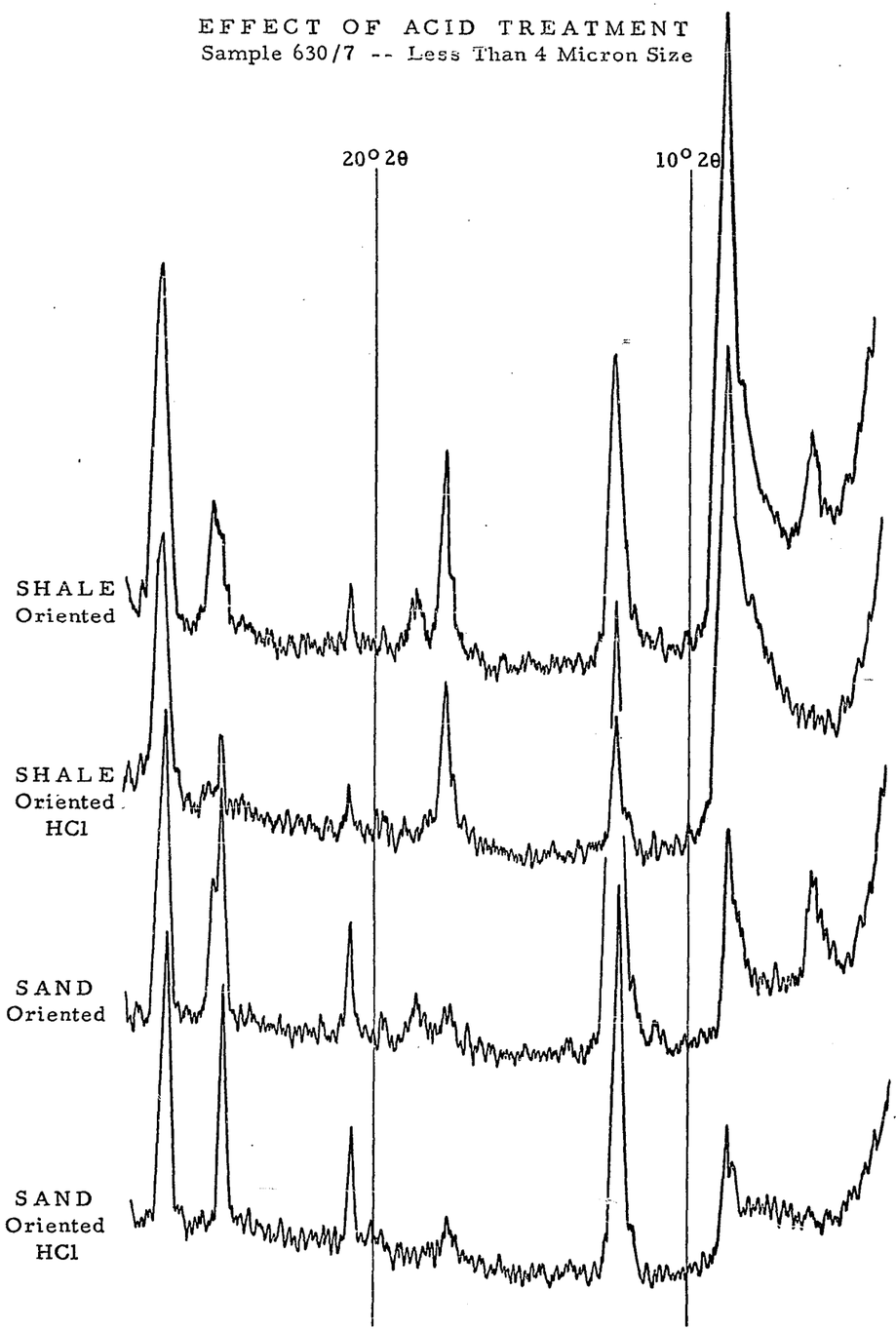
EFFECT OF HEAT TREATMENT
Shale Sample 630/7 -- Less Than 4 Micron Size





EFFECT OF HEAT TREATMENT
Sand Sample 630/7 -- Less Than 4 Micron Size

EFFECT OF ACID TREATMENT
Sample 630/7 -- Less Than 4 Micron Size



employed. Diffraction crystals and electronic controls were varied as necessary for each element.

Results of the chemical analyses, by weight percent, are recorded on the following page.

CHEMICAL ANALYSES

	SiO_2	Al_2O_3	FeO	MgO	K_2O	CaO	P_2O_5	Na_2O	MnO	TiO_2	S	Cl[a]	Ig.Loss[b]	Total
Desmoinesian Shale														
142/9	56.1	19.6	7.93	2.82	4.01	0.28	0.16	1.42	0.14	1.31	0.11	0.18	5.87	99.75
142/15c	53.0	21.9	6.14	1.18	2.58	1.41	0.10	0.74	0.04	1.19	7.21	0.09	9.85	105.34
142/19c	47.8	23.7	9.82	2.17	4.96	0.64	0.27	1.08	0.18	1.08	2.99	0.17	6.97	101.66
106/1	58.4	19.7	8.30	2.97	3.63	0.38	0.16	0.98	0.18	1.04	0.19	0.11	6.78	102.71
630/7	60.5	19.0	5.81	3.47	3.57	0.20	0.13	1.38	0.03	1.28	0.38	0.12	4.76	100.51
360/6	52.8	23.6	7.05	2.60	4.34	0.34	0.15	0.99	0.08	1.06	0.97	0.09	8.23	102.21
278/17	57.8	18.3	3.77	3.77	4.76	5.11	0.18	0.99	0.03	1.16	0.25	0.01	8.93	105.05
627/3a	57.6	23.2	4.50	2.18	4.59	0.18	0.14	1.18	0.04	1.41	0.15	0.01	6.22	101.39
Desmoinesian Sand														
142/9	73.0	12.5	4.12	1.50	1.75	0.18	0.11	1.69	0.04	0.72	0.10	0.23	2.00	97.71
106/6	74.1	7.0	3.44	1.11	0.70	7.96	0.14	0.73	0.15	0.48	0.17	0.08	5.40	101.38
630/7	75.1	11.3	3.92	1.23	1.17	0.91	0.10	1.26	0.03	0.36	0.25	0.05	2.65	98.28
500/3a	76.2	7.6	4.64	1.25	0.73	3.53	0.18	1.11	0.12	1.41	0.52	0.03	2.38	99.67
278/17	55.8	10.6	4.29	3.49	2.74	10.42	0.23	1.40	0.04	0.60	0.51	0.01	9.19	99.31
627/3b	85.9	7.4	3.45	0.83	0.80	0.33	0.10	1.24	0.07	0.54	0.04	0.02	1.66	102.36
Permian Shale														
Fargo/32	51.6	16.7	8.49	8.71	4.81	2.44	0.19	0.92	0.13	0.82	0.03	0.02	8.53	103.37
Permian Sand														
AL3/50	65.0	14.9	5.18	1.65	3.91	0.02	0.06	2.81	0.01	0.32	0.00	0.01	2.66	96.52
Ordovician Shale														
245/1c	52.4	17.3	3.86	5.20	7.64	5.80	0.21	0.62	0.04	0.72	1.64	0.01	7.06	102.49
Ordovician Sand														
316/3a	91.0	3.85	0.00	0.67	0.86	0.00	0.05	0.75	0.00	0.12	0.17	0.23	0.53	98.00
316/24	89.1	3.90	0.00	0.45	1.12	1.01	0.59	0.75	0.00	0.12	0.46	0.27	2.72	100.22

[a]The Cl is not included in the total because it is present as a negative ion.

[b]Ignition losses are determined by heating to 1000° C for 1 hr, the amount recorded is adjusted for the amount of S present.